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THE HYDRATES OF MANGANOUS SULPHATE.

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Water has the faculty of entering into combination with certain chemical compounds, forming the so-called "hydrates." For convenience of reference these hydrates may be divided into three classes, although the lines of division are somewhat dim and arbitrary. Still, a classification may aid us in concentrating our attention and in obtaining precise ideas, thus enabling us to get a better insight into the nature of such compounds.

The first class embraces the hydrates of colloid or non-crystalline substances. When such compounds as silica, the hydroxides of iron, aluminium, etc., pass out of solution, solid non-crystalline masses are formed, containing variable quantities of water. If such hydrates be dried at definite temperatures and pressures, they sometimes have a fixed composition in stoichiometrical ratios. Generally, however, the water contained in them passes off continuously with rise of temperature. Our knowledge of the nature of colloids[1] is so vague that it would be premature to present any general considerations relative to their hydrates. Indeed, the colloid state seems often to depend upon the presence of "hydrate-water." A very interesting and fruitful field of investigation is to be found here, the working of which is very desirable.

The second class comprises the hydrates of the acids, bases, alcohols and the like. Their hydrate-water seems to enter into the intimate constitution of the molecule. In these compounds

[1] See my paper "On the Nature of Colloid Solutions," Am. J. Sci. **43**, 218.

there is generally no outward sign of their containing water, which is bound so firmly that often it cannot be removed without the entire character of the substance being changed. In this class, the "hydrate-water" may not be separated from the acid, base, or alcohol, as the case may be, by the act of solution, and we may perhaps in some cases speak of the hydrates existing as such in solution.

The third class of hydrates takes in those of the salts. Although salts made up of univalent bases and acid radicles do not, with a few exceptions, form crystalline compounds with water, this property is enjoyed to a considerable degree by salts composed of multivalent bases and acid radicles. Double salts also, even if consisting of salts which do not themselves form hydrates, almost invariably crystallize with water.

The above classification is indeed imperfect, yet it permits us to make certain distinctions that are likely to be overlooked. We have no right to apply hypotheses based upon phenomena observed in one class to phenomena observed in another. The existence of hydrates as such in liquid solution is a debated question. Now, nearly all the conclusions favoring the assumption of hydrates in solution are drawn from facts gleaned in the study of the behavior of solutions of hydrates of the second class. Even if hydrates of sulphuric and nitric acids, etc., be shown to exist in solution, it cannot at once be affirmed that hydrates of the third class are also capable of existence in solution. On the other hand, even if the physical constants of solutions of salts are identical, no matter what the hydrate from which the solution is prepared, the conclusion that hydrates of acids, etc., cannot exist in solution does not necessarily follow. Each class of hydrates must be considered by itself; conclusions in regard to one class cannot be extended to another.

The existence of hydrates of the first class in solution—a possibility which seems not to have received much attention—is rendered probable from the fact that most of the dehydrated colloids are quite indifferent towards water; once deprived of water, they become insoluble. As stated above, the colloid state is perhaps dependent upon the "hydrate-water."

The water of crystallization plays much the same rôle as the water of solution. If it be admitted that certain salts be decomposed into their ions when dissolved in water, the conclusion

necessarily follows that such a decomposition is effected by the water of crystallization.[1]

As such an intimate connection prevails between "crystallohydrates" and their saturated solutions, a thorough study of the latter should give important information with regard to the former. Much work has been done upon the subject of solubility, but most of it does not take into consideration the principle that solutions are saturated only with respect to a distinct nucleus. Saturated solutions of hydrates are cases of dynamic equilibrium between a definite hydrate and the solution. As soon as the hydrate changes, the solubility changes also. This principle—first formulated by Ostwald (1885), although Demarçay,[2] in a study of the sulphates of thorium, had shown its necessity—is of fundamental importance. The maximum amount of a salt that can enter into solution depends principally upon the temperature and its state of hydration. The solubilities of the various hydrates of a salt are in general different, and at the temperature where one hydrate changes into another there is a break in the continuity of the curve representing the solubility. The determination of the solubility of salt hydrates accordingly affords a valuable means of ascertaining what are their limits of stability. Determinations of the solubilities of all the hydrates of a salt have been made in but few instances.[3] Although not much that is novel can be expected from the study of further examples, it is nevertheless important to illustrate the principles of the states of equilibrium of heterogeneous systems, of which solutions of hydrates are cases, by as great a variety of examples as possible. The present paper accordingly treats of the hydrates of manganous sulphate throughout their entire range of solubility, giving a general survey of their behavior and limits of stability.

A common way of preparing hydrates consists in driving off water (by heat, exposure in a vacuum to dehydrating substances, etc.) from a higher hydrate, until a compound is obtained in which the quantities of salt and water are in simple stoichiometrical ratio. It is then assumed that the desired hydrate is formed. In reality, however, there is no ground for any such assumption, unless the

[1] See my paper "On the Dissociation of Salts into their Ions by Water of Crystallization," This Journal **14**, 604.

[2] Compt. rend. **96**, 1859 [1883].

[3] Most of these have been done by Bakhuis Roozeboom, and are published in the Zeitschrift für physikalische Chemie.

hydrate has been shown actually to crystallize from its solution; and even then we cannot assume that hydrates formed according to such different methods will have the same properties, for isomeric hydrates are capable of existence. The assumed hydrate may be merely a mixture of the higher hydrate and anhydrous salt or lower hydrate. It is quite probable that a mixture of several hydrates may be formed in such proportions that its composition corresponds to that of a definite hydrate. It is easy to obtain intermediate mixtures containing any desired fraction of a molecule of water, and we have as much right to suppose that we then have a definite hydrate as when we hit upon an integral number of molecules. A true criterion of a fixed hydrate is its capability of crystallizing from solution spontaneously. In the study of the hydrates of manganous sulphate, my first object was to prepare hydrates answering to the above criterion. This was done in two ways: 1. Solutions of the salt were allowed to deposit crystals at different constant temperatures, the amount of "hydrate-water" being a function of temperature, the higher the latter, the less the former. 2. Liquids which have great attraction for water and no chemical action upon manganous sulphate, such as sulphuric acid and alcohol, were added to a solution of the salt, the amount of water of crystallization being thus diminished. Below, under each hydrate are given the methods of preparing it.

A definite hydrate once obtained, the next thing was to determine its solubility; the methods employed and apparatus used are described below under the head of "Determinations of Solubilities."

The solubilities of the hydrates being obtained and curves representing them constructed (Fig. 2), we can compare and discuss them (page 240) and treat of any special points that suggest themselves (page 246).

Dètermination of Solubilities.

The accuracy of a determination of solubility depends largely upon the constancy of the temperature at which a determination is being made. For temperatures between 25° and 60° I made use of a so-called "Ostwald's thermostat." Its temperature during an experiment did not vary more than 0.1°, and not more than 0.2° to 0.3° from day to day. In order to reduce the influence of a change of temperature in the laboratory upon the

temperature of the thermostat, the thermo-regulator was almost wholly immersed in the water contained in the thermostat. The windmill which drove the paddles was made entirely of wood. Such a one is easily constructed out of thin pine paddles set in a hub, and is so stiff and can be so delicately poised that it requires but a very weak current of air to run it. For temperatures between 60° and 180° a large bath of sulphuric acid or of glycerine was employed; between 25° and 0° about three gallons of water were heated or cooled to the desired temperature and used as a bath; below 0°, solutions of common salt were used. By stirring constantly and adding hot water, ice or a mixture of ice and snow, as might be required, it was possible to keep the temperature from varying more than 0.5°.

Equilibrium between the hydrate and its solution was attained in four ways, each being employed throughout a certain range of temperature.

For temperatures below 10°, the hydrate, broken up into small fragments, together with a solution containing about 50 parts of salt to 100 parts of water, was introduced into a small flask, which was set in a bath at the desired temperature. The contents of the flask were well shaken every 15–20 minutes during at least three hours. A sample of the solution was then drawn off by means of a pipette provided with a filtering arrangement, about 10 cc. being taken. This was run into a little glass boat, such as described by Trevor,[1] and the water drawn off. To expel the last traces of water, the salt was heated in the boat to 160°–170° in an air-bath.

The apparatus sketched in Fig. 1 was used in the determination of solubilities between 10° and 60°. *AB* is a glass tube having a length of 5 inches and an internal diameter of about 0.8 inch. At its bottom the tube *e* is melted in, which establishes communication with the tube *C*. A bit of rubber tubing is slipped over one end of *e* at *t*, into which passes easily but tightly the glass rod *pa*. In making a determination, a little wad of cotton-wool is placed in the projecting part of the bit of rubber tubing, and the rod *pq* pressed down upon it, the cotton acting as a filter. Coarsely-powdered hydrate is now put into the tube *AB*, and enough of a solution of manganous sulphate of about 50 per cent. to fill the tube a little more than half. The stirrer *rs*, a piece of

[1] Ztschr. phys. Chem. **7**, 468 (1891).

stout platinum wire, is put in position and the cork *D* inserted. After the tube *C* has been attached, the apparatus is put in the thermostat and its contents stirred frequently. After three or four hours, the solution is allowed to settle and the rod *pa* raised. By means of a suction-pump connected to the tube *xy*, the clear solution is drawn over into *C*. A portion of this is poured into a glass boat and the water driven off as described above.

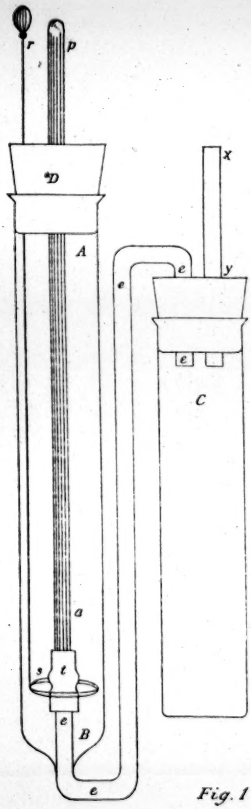


Fig. 1

It is impossible to employ either of the above methods in determining the solubility of the monohydrate, the only hydrate stable above 60°. Therefore the following procedure had to be adopted for temperatures up to 100°. A weighed quantity of a solution of manganous sulphate of known concentration was evaporated on the water-bath until the monohydrate just began to separate out. The flask was then removed from the bath, and, after its neck was carefully wiped dry on the inside, weighed. At the temperature of the laboratory, the monohydrate soon entered into solution. The clear solution was now heated to 100°, this time with the flask tightly corked. Invariably the separation of the hydrate ensued so soon as the solution attained the temperature of the bath. A slight calculation gives the solubility of the hydrate at 100°. For temperatures lower than 100° more of the water was driven off, the solution allowed to stand until the precipitated

hydrate had again dissolved, and the clear solution heated in a bath of glycerine, a little mono-hydrate being thrown in from time to time to avoid supersaturation. The temperature at which the hydrate appeared was, for a definite concentration, a fixed one.

The solubility above 100° was determined by heating solutions of known concentration in sealed hard-glass tubes until a separation of solid took place.

Modes of Expressing Solubilities.

Although the principal phenomena of solubility had been known from earliest times, no really scientific investigation was carried out before the year 1819, when Gay Lussac published a paper on the subject,[1] in which he gave his results a graphical representation. The curves were so constructed that temperatures were laid off along the axis of abscissæ, and the number of parts of substance dissolved in 100 parts of water was measured on the axis of ordinates. Gay Lussac was probably led to adopt this method of representation in order to shape his results to practical ends. The example thus set has been followed by almost all who have occupied themselves with the question of solubility. But with this mode of representation the determinations in aqueous solution are confined within rather narrow limits, *viz.*, 0° and 100°. But below 0° and above 100°, substances can still be held in solution. Hence a need arises for another mode of representation not subject to these limitations. Étard seems to have been the first to propose a new mode of graphical representation.[2] Instead of taking as ordinate the amount of substance that 100 parts of water can dissolve, he takes the quantity of substance contained in 100 parts of the saturated solution. Thus, one of the values is a function of the other; when the quantity of substance increases, the quantity of solvent decreases, and all the results are comparable, being comprised between 0 per cent. and 100 per cent. of dissolved substance. The results when plotted give straight lines, and if an interpolation formula be made it takes the form

$$y''_{t_0} = a + bt_0,$$

where y''_{t_0} indicates the solubility between t_0 and t', a the ordinate of solubility at the origin, and b the coefficient of solubility for every degree.

[1] Ann. chim. phys. [2] **11**, 296. [2] Compt. rend. **98**, 993; 1276; 1432; **104**, 1614.

It must be said that this "straightness" of the curves is in a measure due to the choice of the values of ordinates and abscissæ. The curves never have any considerable inclination towards the axis of ordinates, and curved lines are easily smoothed down into approximately straight lines. The curve is a branch of a hyperbola, which is practically straight for moderate concentrations. Still this mode of representation is valuable, inasmuch as it shows clearly how solution passes into fusion.

A more rational mode of expressing solubilities is by the use of molecular numbers, for these only are chemically comparable. There are two ways that may be employed: (1) The ratio of the number of molecules of dissolved substance to any number (generally 100) molecules of the solvent; (2) the ratio of the number of molecules of dissolved substance to any arbitrary (usually 100) number of molecules of the solution. The second of these two methods seems to be peculiarly adapted to the representation of the relations of the physical constants of solutions of various salts.

As my object in determining the solubilities of the hydrates of manganous sulphate was simply to get information as to their limits of stability, I have employed the mode proposed by Gay Lussac, which shows clearly the changes undergone by the different hydrates at different temperatures.

Hepta-hydrate: $MnSO_4.7H_2O$.

If a solution containing from 60 to 70 parts manganous sulphate to 100 parts water be exposed to a temperature below 5°, a mass of pinkish monoclinic crystals soon separates out, which possess the formula $MnSO_4.7H_2O$. The appearance and properties of the hepta-hydrate have been described by Brandes[1] and Carnot.[2] It has been found in "crystalline masses with fibrous structure" in Utah, being known as the mineral Mallardite. It loses some of its water of crystallization at rather low temperatures; thus Brandes states that it became soft at 12°, and a viscous liquid at 18°, while at 24° it turned into a white, porridge-like mass. This behavior is undoubtedly due to its changing into hydrates containing less water of crystallization.

Two series of determinations of its solubility were made, one from —10° to 7°, the other from —10° to 58°. In the second series the hydrate was heated with its solution in a flask slowly and con-

[1] Ann. der Phys. Pogg. **20**, 578. [2] Bull. Soc. Min. **2**, 117.

tinuously, samples of the solution being removed after every five degrees rise in temperature. The results are given in Tables I and II; those of I being represented graphically in Fig. 2 (curve 7, 7).

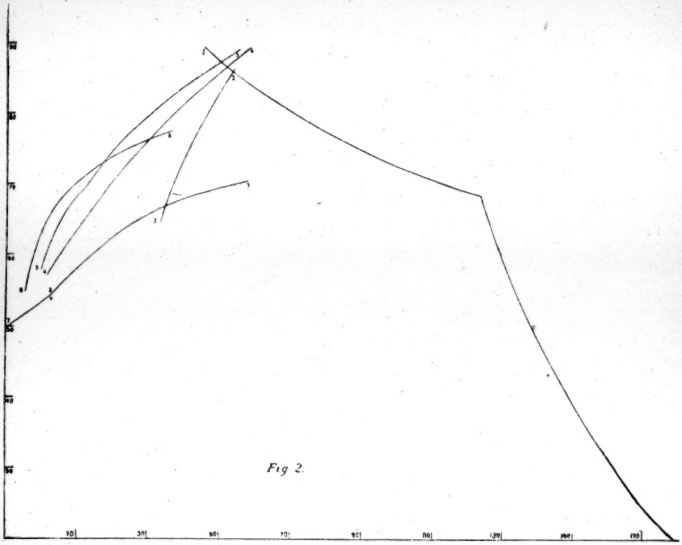


Fig 2.

TABLE I.

Solubility of $MnSO_4.7H_2O$. — *Series* 1.

Temperatures,	−10°	−8°	−5°	0°	5°	7°
Parts $MnSO_4$ to 100 parts H_2O,	50.11	50.93	51.53	53.61	54.83	56.62

TABLE II.

Solubility of $MnSO_4.7H_2O$. — *Series* 2.

Temperatures,	−10°	−5°	0°	5°	10°	15°
Parts $MnSO_4$ to 100 parts H_2O,	50.24	51.71	53.46	54.73	59.91	64.34

Temperatures,	20°	25°	35°	45°	54°	58°
Parts $MnSO_4$ to 100 parts H_2O,	66.61	67.14	68.51	70.33	73.06	72.94

Hexa-hydrate: $MnSO_4.6H_2O$.

It was remarked by Brandes[1] that the hepta-hydrate, if allowed to stand at temperatures in the neighborhood of 10°, gradually loses one molecule of water, being converted into the hexa-hydrate. I have found that a warm solution of manganous sulphate containing about 80 per cent. of the anhydrous salt, when cooled to 2°–5°, deposits small hexagonal plates, the composition of which corresponds to the formula $MnSO_4.6H_2O$. By sowing some of the crystals thus obtained in a solution maintained at 0°, large, well-formed crystals separate out.

The solubilities of the hexa-hydrate are given in Table III, and graphically in Fig. 2 (curve 6, 6).

TABLE III.

Solubility of $MnSO_4.6H_2O$.

Temperatures,	−4°	0°	3°	5°	9°	15°
Parts $MnSO_4$ to 100 parts H_2O,	55.87	64.21	66.87	67.49	70.88	72.45
Temperatures,	20°	25°	30°	34°	35°	38°
Parts $MnSO_4$ to 100 parts H_2O,	74.35	75.38	76.24	77.02	77.23	78.41

Penta-hydrate: $MnSO_4.5H_2O$.

Solutions of manganous sulphate evaporated at 10°–15° deposit triclinic crystals of the penta-hydrated salt. It was obtained by Brandes by the abstraction of two molecules of water from the hepta-hydrate by the action of absolute alcohol.

In Table IV are given the results of the determinations of the solubility of the penta-hydrate, which are represented graphically in Fig. 2 (curve 5, 5).

[1] *Loc. cit.*

TABLE IV.

Solubility of $MnSO_4.5H_2O$.

Temperatures,	0°	2.5°	4°	7°	10°	15°
Parts $MnSO_4$ to 100 parts H_2O,	58.05	62.41	64.22	66.83	68.05	72.33
Temperatures,	20°	25°	30°	32°	34°	37°
Parts $MnSO_4$ to 100 parts H_2O,	75.16	78.63	79.16	80.38	82.04	83.91
Temperatures,	40°	42°	45°	47.7°	53°	54°
Parts $MnSO_4$ to 100 parts H_2O,	84.63	85.27	86.16	86.95	88.89	89.08

Tetra-hydrate: $MnSO_4.4H_2O$.

It is in the form of the tetra-hydrate that manganous sulphate comes upon the market. This is due to the fact that this hydrate separates out of its solution at ordinary temperature (18°–20°). It was obtained by Brandes[1] by the decomposition of higher hydrates by the action of alcohol and heat.

An excellent method for obtaining it rapidly is the following: A strong solution of manganous sulphate is shaken up well with half its volume of strong alcohol. On standing, the solution promptly separates into two layers, in the lower of which crystals soon appear. After a few hours an abundant crop of crystals is obtained which have the same solubility as those crystallized from aqueous solution alone.

The results of the determinations of its solubility are given in Table V, and represented graphically in Fig. 2 (curve 4, 4).

TABLE V.

Solubility of $MnSO_4.4H_2O$.

Temperatures,	2.2°	7.3°	11°	15°	20°	25°	
Parts $MnSO_4$ to 100 parts H_2O,	57.88	61.78	64.01	67.12	69.93	72.33	
Temperatures,	30°	35.5°	40°	45°	48°	52°	56°
Parts $MnSO_4$ to 100 parts H_2O,	74.67	78.81	79.63	83.06	84.33	86.16	88.19

[1] *Loc. cit.*

Tri-hydrate: $MnSO_4.3H_2O$.

Graham states that "a crystalline crust of sulphate of manganese, deposited from a warm solution, was found to contain three atoms of water." No other mention, so far as I know, has been made by any investigator of the spontaneous crystallization of the tri-hydrate from solution. Brandes[1] affirms that he obtained the tri-hydrate by the decomposition of other hydrates. Thus by boiling absolute alcohol over the hepta-hydrate as well as over the tetra-hydrate, he succeeded in reducing the number of molecules of water combined with the salt to three. I myself have found that if 98-per cent. alcohol be poured over the tetra-hydrate, and the whole be allowed to stand at $\pm$ 20°, the clear crystals of the tetra-hydrate gradually become opaque and fall apart to form a powder. An analysis made at the end of a month gave results corresponding with the formula $MnSO_4.3H_2O$. I made a couple of determinations of the solubility of the hydrate thus obtained, finding them to coincide with those made with the tri-hydrate as described below. Brandes assumes that the tri-hydrate is formed when the tetra-hydrate is exposed in a vacuum for some time to the dehydrating action of sulphuric acid or calcium chloride.

Brandes' statement that dehydrated manganous sulphate gradually absorbs three molecules of water from the air, I can in nowise corroborate. In general it may be said that the amount of water that a dehydrated salt can absorb from the air is a function of the temperature and the hygroscopic condition of the atmosphere; the higher the temperature and the drier the air, the less the quantity of water taken up by the salt. If at ordinary temperatures the salt be exposed to an atmosphere always saturated with aqueous vapor, it will in time absorb enough water to dissolve itself. It is accordingly inaccurate to affirm that a definite hydrate is formed. True, the conditions of moisture and temperature may be such that the salt will after a time lose about as much water as it absorbs, and the composition of the mixture may correspond to that of a definite hydrate, but we cannot therefore conclude that such a definite hydrate has been formed. To illustrate these considerations in the case of manganous sulphate, a weighed quantity of the carefully dehydrated salt was put on a watch-glass placed on a support in a large beaker. Some water was poured into the beaker, which was then tightly closed with a glass plate. The salt was

[1] *Loc. cit.* p. 574.

thus exposed to an atmosphere saturated with aqueous vapor. The beaker was then set in a place where the temperature did not vary much from 20°, and the watch-crystal and its contents weighed from time to time. Table VI gives the weights after the times specified.

TABLE VI.

Absorption of Moisture by $MnSO_4$.

Hours,	0	3	20	43	60	110
Weight of salt in grams,	2.4176	2.4561	2.6173	2.8285	3.4126	4.9108

After about 100 hours, enough water had been absorbed to dissolve the salt.

The tri-hydate is formed on slowly heating a solution over the hepta-hydrate above 7° up to 35°. It is easily obtained in quadratic crystals by allowing a solution to evaporate at 33°–35°.

Table VII gives the results of the determinations of its solubility, which are represented graphically in Fig. 2 (curve 3, 3).

TABLE VII.

Solubility of $MnSO_4.3H_2O$.

Temperatures,	5°	12°	16°	19°	25°	30°
Parts $MnSO_4$ to 100 parts H_2O,	54.68	60.56	63.41	65.12	66.85	67.38
Temperatures,	35°	40°	48°	53°	57°	
Parts $MnSO_4$ to 100 parts H_2O,	68.31	70.63	71.89	72.81	73.17	

Di-hydrate: $MnSO_4.2H_2O$.

By heating the hepta-hydrate slowly with 55-per cent. alcohol to about 80°, Brandes[1] states he got a "weissen, opaken Krystallmehl," which had a composition corresponding to that of the di-hydrate. I regard it as doubtful, however, that the di-hydrate can exist at that temperature. Probably he did not succeed in removing all moisture from the compound before analyzing it.

The di-hydrate may easily be obtained in rhombic crystals by evaporating a solution of manganous sulphate on a water-bath until a crust begins to form on the top. It is then exposed to the temperature $\pm 43°$ in the thermostat. The solution must be

[1] *Loc. cit.*

stirred from time to time so that the pinkish crust that forms may be made to settle to the bottom. By sowing some of these crystals in a solution at 40°–45°, well-formed crystals can be obtained.

The di-hydrate was also obtained as a pinkish powder by the action of strong sulphuric acid upon solutions of manganous sulphate. If sulphuric acid (sp. gr. 1.83) be carefully run upon an equal volume of a 70-per cent. solution of manganous sulphate in alcohol, a precipitation of a pinkish-white powder takes place. The mixing of the acid and alcohol must take place slowly—by diffusion alone—that too much heat be not evolved. After two or three days the separation of the di-hydrate is completed. The solution is then filtered through glass-wool with the aid of a suction-pump, and the precipitate washed with 50-per cent. alcohol. A determination of water in the hydrate (which was well dried by pressing between folds of filter-paper) gave 19.54 per cent. H_2O, while the di-hydrate contains 19.21 per cent. The solubility of the di-hydrate is given in Table VIII, and represented graphically in Fig. 2 (curve 2, 2).

TABLE VIII.

Solubility of $MnSO_4.2H_2O$.

Temperatures,	35°	40°	42°	45°	50°	55°
Parts $MnSO_4$ to 100 parts H_2O,	68.88	75.31	77.63	80.07	83.16	86.27

Mono-hydrate: $MnSO_4.H_2O$.

Solutions of manganous sulphate containing more than 70 per cent. of salt deposit at temperatures from 60° to 70° a whitish solid. Thus it is that on boiling solutions of manganous sulphate they become turbid from the separation of solid matter. Analysis proves this compound to be the mono-hydrate. The fact that manganous sulphate is more soluble at temperatures below 60° than at temperatures above that point has been known for a long time. The first analysis of the precipitate was made by Kühn;[1] Étard[2] also gives the results of an analysis.

By boiling the tetra-hydrate with 90-per cent. alcohol, the mono-hydrate is easily obtained as a pinkish-white powder. It is diffi-

[1] J. prakt. Chem. **61**, 239. [2] Compt. rend. **106**, 208.

cult to separate it from its aqueous solution, the solution being so thick and the precipitate so fine that filtration is out of the question. The mono-hydrate was also obtained in the following way: A 70-per cent. solution of manganous sulphate was heated in the thermostat to 47°, and an equal volume of 98-per cent. alcohol added. Two layers soon separated out;[1] in a day or so a quantity of hard pinkish crusts were deposited in the lower layer, and these consisted of the mono-hydrate.

The results of the determination of its solubility are recorded in Table IX, and shown graphically in Fig. 2 (curve 1, 1).

TABLE IX.

Solubility of $MnSO_4.H_2O$.

Temperatures,	48°	53°	65°	72°	78°
Parts $MnSO_4$ to 100 parts H_2O,	87.98	86.10	84.33	82.73	79.13
Temperatures,	90°	100°	106°	115°	117°
Parts $MnSO_4$ to 100 parts H_2O,	75.63	71.27	70.14	69.78	68.81

Dehydrated Manganous Sulphate.

Étard[2] has determined the solubility of dehydrated manganous sulphate from —8° to 57°. At —8°, "le sulphate de manganèse anhydre et l'eau sont dans le rapport moleculaire $SO_4Mn : 19H_2O$; à 57°, on a $SO_4Mn : 9H_2O$." Now my determinations of the solubility of the hepta-hydrate at —8° show the anhydrous salt and water to be in the molecular ratio $MnSO_4 : 19H_2O$; and at 57°, if the determination be made with solution over the tri-hydrate, the ratio is $MnSO : 10H_2O$. These results agree with those of Étard, and the cause of the agreement is not far to seek. Anhydrous manganous sulphate rapidly takes up seven molecules of water at —8°; Étard's determination then is that of the hepta-hydrate. As stated above (p. 236), the hepta-hydrate easily decomposes into the tri-hydrate, so that Étard's determination at 57° was with the tri-hydrate. His method of determining solubilities[3] is such that it

[1] It is noteworthy that the color of the lower layer was much less intense than that of the original solution, showing that the electrolytic dissociation was not so great as before.

[2] Compt. rend. **106**, 208.

[3] Sur la Solubilité des Sels: Conference faite au laboratoire de M. Friedel, 1888-1889, page 136.

is possible for such changes in the amount of water of crystallization to occur. Now if it be remembered that Étard expressed the results of his determinations of solubility in parts of salt to 100 parts of saturated solution, and that the effect of such a mode of representation is to straighten out curves, it is apparent that his results coincide closely with mine as given in Table II.

In Table X are given the results of the determinations of the solubility of anhydrous manganous sulphate which are platted in Fig. 2.

TABLE X.

Solubility of the Dehydrated Sulphate.

Temperatures,	120°	132°	141°	146°	155°	170°
Parts $MnSO_4$ to 100 parts H_2O,	67.18	63.16	41.18	38.83	26.49	16.15

Discussion of Curves (Fig. 2).

The curves of solubility of the hydrates of manganous sulphate regarded collectively present certain peculiarities. One which at once attracts the attention is that five of them are concave towards the axis of abscissæ. Consequently, the solubilities of the hexa-, penta-, tetra-, tri- and di-hydrates do not increase so rapidly as the temperature. On the other hand, the curves of the mono-hydrate and anhydrous salt are convex towards the axis of abscissæ, their solubility diminishing less rapidly than the temperature rises. The curve of solubility of the hepta-hydrate appears to be very slightly convex towards the axis of abscissæ. This concavity of the curves towards the axis of abscissæ has been found to occur but rarely in the salts hitherto investigated.

Another peculiarity is the relative position of the curves. Considering the hexa-, penta-, tetra- and tri-hydrates, we observe the more water of crystallization the hydrate contains, the greater its solubility. Now the contrary is generally the case with the different hydrates of other salts examined up to date.

Manganous sulphate has the property of uniting with water to form "crystallo-hydrates" between the temperatures —10° and 117°; below the former temperature, a mechanical mixture of the hepta-hydrate and ice separates out; above the latter temperature, only the anhydrous salt is capable of existence. As the amount of water of crystallization in the hydrates seems in the main to depend

upon the temperature, this interval of 127° may be divided into seven intervals, to each of which one of the hydrates corresponds. These we shall call the intervals of stable existence, or of stability of the hydrates. They are characterized by two circumstances: 1. A solution of manganous sulphate, kept at a temperature within one of these intervals, deposits the corresponding hydrate; 2. Any hydrate put with its solution at a temperature comprised within the limits of an interval of stability, passes more or less rapidly into the hydrate corresponding to the interval. Of course, the limits of these intervals of stability can be only roughly outlined, no sharp lines of demarcation existing between them; yet this conception of an interval of temperature in which a single hydrate is stable introduces a certain order which facilitates greatly the study of the hydrates. The limits of each of the hydrates are as follows:

For the	hepta-hydrate,	−10° to	−5°,
" "	hexa-hydrate,	− 5° to	+8°,
" "	penta-hydrate,	8° to	18°,
" "	tetra-hydrate,	18° to	30°,
" "	tri-hydrate,	30° to	40°,
" "	di-hydrate,	40° to	57°,
" "	mono-hydrate,	57° to	117°.

It might be well before passing to the consideration of each of these hydrates, to make a few general remarks about heterogeneous systems and Gibb's rule of phases, of which this investigation is an illustration. Our heterogeneous system consists of the two definite compounds, manganous sulphate and water. If we consider a hydrate, the tri-hydrate, for instance, in equilibrium with its solution at a certain temperature, say 30°, we have three phases of the system before us. These are (1) aqueous vapor (gaseous); (2) solution (liquid); (3) tri-hydrate (solid).

At 37°, however, the tri-hydrate decomposes into water and the di-hydrate. 37° marks, therefore, a quadruple point of transition, where four phases can coexist, which are (1) aqueous vapor (gaseous); (2) solution (liquid); (3) tri-hydrate (solid); (4) di-hydrate (solid).

Similar considerations obtain for the other hydrates. Wherever two curves cross one another, there are four phases present, and a quadruple point of transition is thereby marked. In the

example above cited we have passed along the curve of the tri-hydrate until we arrived at the curve of the di-hydrate. There is, however, a quadruple point of transition between the mono-hydrate and tri-hydrate, occurring when the tri-hydrate is rapidly heated. There is a distinction to be made between these two points of transition; the one between the di- and the tri-hydrate is reversible, while the one between the mono- and the tri-hydrate is irreversible. That is, we arrive at the same point no matter whether we pass up the curve of the tri-hydrate or pass down the curve of the di-hydrate, while we arrive at the point of transition of the tri-hydrate and the mono-hydrate, only in passing up the curve of the tri-hydrate. The mono-hydrate does not pass directly into the tri-hydrate. Examples of irreversible points of transition are common with the hydrates of salts which possess a considerable stability.

The curve of solubility of the hepta-hydrate was determined from —10°, the cryohydratic point, to 7°, the temperature at which the hydrate ceases to be capable of existence. On heating the hepta-hydrate, partial melting occurs, that is, the hydrate loses water and is converted into lower hydrates. If the curves of solubility of the hexa-, penta-, and tetra-hydrates be prolonged downwards, they cut the curve of the hepta-hydrate at —5°, —2° and 0° respectively. All these temperatures are, however, within the interval of stable existence of the hexa-hydrate. The penta-hydrate at —2°, and the tetra-hydrate at 0°, are then in mobile equilibrium, both tending to pass into the hexa-hydrate. So soon as the hepta-hydrate might become changed into the penta- or tetra-hydrate, the latter would at once pass into the hexa-hydrate. Brandes[1] observed that at temperatures about 6° the hepta-hydrate decomposed into the hexa-hydrate: a fact entirely in accordance with the above statements. The upper limit of existence of the hepta-hydrate touches the curve of the tri-hydrate; the hepta-hydrate there decomposes into four molecules of water and the tri-hydrate. It must not be inferred, however, that the tetra- and penta-hydrates cannot be obtained by the decomposition of the hepta-hydrate, for such a transformation often takes place. But the transformation is not direct, that is, the hepta-hydrate does not lose all at once two or three molecules of water, as the case may be. If the hepta-hydrate with its solution be exposed to the tem-

[1] *Loc. cit.*

perature of 20°, the tetra-hydrate is finally obtained. The transformation may proceed in two ways: 1. The hepta-hydrate is converted into the hexa-hydrate, this into the penta-hydrate, and this finally into the tetra-hydrate; or, 2. the hepta-hydrate may be decomposed directly into the tri-hydrate, which then takes up a molecule of water, since it is in the interval of stable existence of the tetra hydrated salt. The product of the decomposition depends chiefly upon the interval of stability taken. Similar considerations are applicable for the transformation of the hepta-hydrate into other hydrates.

The hexa-hydrate seems to be incapable of existence at temperatures below —5°, the point at which its solubility crosses that of the hepta-hydrate. From this point, the curve rises rapidly at first, then more and more slowly. At temperatures from 30° to 35° it decomposes rapidly into the tetra-hydrate. As these temperatures are within the limits of the interval of the tri-hydrate's interval of stability, one would expect that the tri-hydrate would be the product of its decomposition. There seems to be a great reluctance, however, on the part of the hexa-hydrate to pass into the tri-hydrate; it seems to be easier for it to become converted into the tetra-hydrate, even when this hydrate is not in its interval of stability. Perhaps the considerable difference of solubilities is of influence on the kind of transformation undergone.

The curve of solubility of the hexa-hydrate cuts that of the penta-hydrate at 15°, a temperature within the interval of stability of the latter hydrate. The hexa-hydrate should yield the penta-hydrate then, if kept long enough at that temperature, and such has been found to be actually the case. A solution of the hexa-hydrate was maintained at 14°–15°, and samples of the crystals removed from day to day and analyzed. The amount of water of crystallization found did not correspond to that of the penta-hydrate until the seventeenth day.

The penta-hydrate and the tetra-hydrate at temperatures near zero pass into the hexa-hydrate. To determine the rapidity with which this transformation takes place, solutions of the penta- and of the tetra-hydrate were exposed side by side to the temperature of melting ice. These were shaken frequently and their concentrations determined (1) after three hours, (2) after six hours, (3) after nineteen hours, (4) after thirty hours. The concentration of each did not coincide with the solubility of the hexa-hydrate until after 20–30 hours.

The curves of solubility of the penta-hydrate and of the tetra-hydrate are nearly parallel, not crossing each other at any point. This indicates that there exists some similarity in the relations of these hydrates to the other hydrates. As stated above, both pass with about the same velocity into the hexa-hydrate at temperatures near zero. Likewise, at temperatures above 35° both easily pass into the di-hydrate. By heating a saturated solution of the penta-hydrate rapidly, it does not decompose into the mono-hydrate before the temperature 58° is reached; similarly, the tetra-hydrate may be heated to 61° before the mono-hydrate appears. In no case have I observed that either the tetra-hydrate or the penta-hydrate became converted into the tri-hydrate.

As might be expected, the tetra- and penta-hydrates are mutually transformable only with great difficulty. A solution of the penta-hydrate was kept at 25° for a couple of weeks without the hydrate's losing water of crystallization. On raising the temperature to 30°, the transformation was complete in 50 hours. This shows that such a transformation is possible only at the upper limit of the interval of stable existence of the tetra-hydrate. In like manner, the conversion of the tetra-hydrate into the penta-hydrate is possible only at the lower limit of the interval of stability of the penta-hydrate. Thus, by maintaining a solution of the tetra-hydrate at 9°–10°, I found the concentration of the solution after a week or so to coincide with the solubility of the penta-hydrate. This want of readiness on the part of the penta- and the tetra-hydrate to pass into each other is further illustrated by the facts that, if crystals of the tetra-hydrate be sown in a supersaturated solution of manganous sulphate at 13°–14°, the tetra-hydrate crystallizes out, although the temperature is within the limits of stability of the penta-hydrate; and if crystals of the penta-hydrate be sown in a supersaturated solution, even at so high a temperature as 25°–26°, a growth of the crystals of the penta-hydrate occurs. After some time, however, the hydrates belonging in the intervals of stability are formed.

The solubility of the tri-hydrate is less than that of the three next higher hydrates, and its curve is seen to be quite independent of theirs, not crossing them at all. There are, then, no points of transition between the hexa-, penta-, and tetra-hydrates and the tri-hydrate, and this is the reason why the latter hydrate does not pass into the penta- or the tetra-hydrate at all easily, and why the

hexa-hydrate at higher temperatures breaks up into the tetra-hydrate rather than into the tri-hydrate. At temperatures within the interval of stable existence of the hexa-hydrate, however, the tri-hydrate passes rapidly into that hydrate. The di-hydrate transforms itself so readily into the tri-hydrate, when it is within the interval of stable existence of this hydrate, that its solubility could be determined only down to the temperature 35°. From this point its curve of solubility rises rapidly to 57°, where the mono-hydrate appears. Not being capable of existence within the intervals of stability of the hydrates higher than the tri-hydrate, its curve has no relations with theirs.

The curve of solubility of the mono-hydrate is essentially different from the curves of the other hydrates, since the mono-hydrate is more soluble in cold than in hot water. I have not been able to determine its solubility at temperatures below 40°, because higher hydrates promptly separate out from such concentrated solutions. In more dilute solutions, the transformation of the mono-hydrate takes place more slowly. Thus, a solution of manganous sulphate was evaporated at 100°, until a quantity of the mono-hydrate had separated out. This was exposed to a temperature of 18°–20°. In a few days, rhombic crystals of the tetra-hydrate appeared, which grew gradually while the amount of the mono-hydrate diminished. As the transformation proceeded, the white, powdery mono-hydrate collected together so as to form ill-defined rhombs, which finally became regular and transparent. The directive force of the act of crystallization made the loose powder assume the geometrical form characteristic of the tetra-hydrate.

At 117° the mono-hydrate loses its water of crystallization, and above that temperature the anhydrous salt is alone stable. The curve expressing its solubility is very steep and convex towards the axis of abscissæ, which it cuts at about 180°. Above this temperature, then, manganous sulphate is insoluble in water. Étard[1] has indeed found "qu'une solution de sulphate de manganèse chauffée à 180° ne contient plus que des quantités negligeables matière en solution." Anhydrous manganous sulphate combines with one molecule of water of crystallization with great ease. Thus, crusts of the dehydrated salt were added to a solution kept at 60° and of such a concentration that the mono-hydrate just

[1] Compt. rend. **106**, 208.

began to separate out; the crusts fell apart very soon to form the characteristic powdery mono-hydrate, as proven by analysis. The combination of the anhydrous salt with more molecules of water than one, takes place with much more difficulty.

It is interesting to follow out the changes in the direction of the curves due to the combination of molecules of water with the anhydrous salt to form hydrates. Thus, beginning at 180°, as the temperature falls, manganous sulphate rapidly enters into solution. At 117° the anhydrous salt combines with one molecule of water, and immediately there is a break in the continuity of the curve. The solubility of the mono-hydrate also increases with falling temperature until the temperature 57° is attained. Here the di-hydrate appears, and the direction of the curve changes completely, the solubility decreasing as the temperature falls. Passing down the curve of solubility of the di-hydrate we arrive at the temperature 37°, where another molecule of water adds itself to the di-hydrate and we have to do with the curve of solubility of the tri-hydrate. This ends at 7°, where it joins the curve of the hepta-hydrate. The curve of the hepta-hydrate ends at —10°, the cryohydratic point.

The general course of these curves resembles the theoretical curve of solubility given by Le Chatelier.[1] It is to be observed that we have not found it necessary in passing from the anhydrous to the hepta-hydrated salt, to take into consideration the hexa-, penta-, or tetra-hydrates. They seem to occupy a position apart from the others. Accordingly, we have two sets of curves: one composed of the hepta-, tri-, di-, and mono-hydrates, and the other of the hexa-, penta-, and tetra-hydrates. These two sets seem to be quite independent of each other.

Supersaturated Solutions.

The term "saturation" is indefinite unless referred to a distinct nucleus, which may be a hydrate or an anhydrous substance. Saturation is not a property of solutions, but a state of equilibrium between solid and solution. Supersaturation is therefore a relative term. A solution may be supersaturated with respect to one hydrate of a salt, and "undersaturated," if such an expression be allowable, with respect to another. The hydrates of manganous

[1] "Recherches experimentelles et théoriques sur les équilibres chimiques," page 139. See also Ostwald's "Lehrbuch der Chemie," **1**, 1057.

sulphate illustrate well these statements. At 10°, for instance, it is possible to prepare four different solutions, saturated with hexa-, penta-, tetra- and tri-hydrate respectively. A solution containing between 68 and 70 parts of salt is supersaturated only with respect to the penta-, tetra- and the tri-hydrates. A solution containing 65 parts of the salt is supersaturated only with respect to the tetra- and tri-hydrates. If now a crystal of any of these three lower hydrates be introduced into a saturated solution of the hexa-hydrate, a separation of crystals of the hydrate added should occur. Accordingly, a solution saturated with the hexa-hydrate should, if a crystal of the penta-hydrate be thrown into it, deposit the penta-hydrate. The weakened solution would now dissolve more of the hexa-hydrate, and this would continue until all the hexa-hydrate was converted into the penta-hydrate. Similar considerations obtain for the other hydrates.

But we have left out of consideration the influence of temperature. The transformation of the hexa-hydrate into the penta-hydrate is possible only when the solution is at a temperature within the interval of stable existence of the penta-hydrate. If it be at a temperature comprised in the interval of the hexa-hydrate, the penta-hydrate may indeed at first crystallize out, but it will soon unite with a molecule of water, and nothing but hexa-hydrate will be present. Also, if a crystal of the penta-hydrate be sown in a solution of the hexa-hydrate, and the whole at once be raised to a temperature within the interval of stability of the di-hydrate, whatever penta-hydrate that may have formed, as well as all the hexa-hydrate, will change into the di-hydrate.

Heat of Solution.

A most important law having reference to the relation of temperature to solubility was enunciated at about the same time by Le Chatelier[1] and by van't Hoff.[2] It states that the solubility of substances which dissolve "in saturated solution" with absorption of heat increases with rise of temperature, while it diminishes with rising temperature if heat is evolved in the act of solution. Its mathematical expression is

$$\frac{dp}{dT} = \frac{\rho}{Tv},$$

in which p represents the osmotic pressure which is approximately

[1] Compt. rend. **100**, 441 [2] Arch. néerland. **20**, 53.

proportional to the concentration,[1] T the absolute temperature, ρ the heat of solution, and v the volume of the solution.

According to this law, the heat of solution of manganous sulphate should be positive for the mono-hydrate, and negative for the other hydrates. This conclusion can easily be verified in the case of the mono-hydrate.

Thomsen[2] has found that the tetra- and penta-hydrates dissolve in water with evolution of heat:

$$\text{"}MnSO_4 + 5H_2O + 400\,H_2O = +\,40\text{ c.}$$
$$MnSO_4 + 4H_2O + 400\,H_2O = +\,1770\text{ c."}$$

and calls particular attention to this unusual case. But a fundamental distinction must be made between the various meanings of the term "heat of solution." The true heat of solution is the heat given out or taken in when a solution passes from a state of saturation at a certain temperature to a state of saturation at a temperature infinitely near the other. This is the heat of solution for which the above law holds good. If more water be added to the saturated solution, heat may be evolved or absorbed, and we have to do with the heat of dilution. Now the true heat of solution may be negative and the heat of dilution positive. In that case there must be a concentration for which no heat is evolved or absorbed when a fresh portion of substance enters into solution. Thus it is possible to dissolve a substance in such a quantity of solvent that the heat effect is *nil*. In the above thermochemical determinations of Thomsen, the hydrates are dissolved in such a quantity of water that further dilution does not bring about a thermal change. In the majority of salts the heat of dilution is small compared with the heat of solution. Just the opposite behavior is observed in the case of the penta- and tetra-hydrates of manganous sulphate. Their true heat of solution is undoubtedly negative, while their heat of dilution is positive. Accordingly, by diluting a saturated solution of either of these hydrates, at a certain point the sign of the heat that comes into play changes from negative to positive. I have found that a solution of the sulphate containing 70 parts of anhydrous salt to 100 parts of water (the concentration of a saturated solution of the tetra-hydrate at 20°) when exposed to temperature of 25°, dissolves more of the tetra-hydrate with a slight absorption of heat, a result entirely in accordance with the above law.

CHICAGO, *January*, 1893.

[1] See, however, Ztschr. phys. Chem. **9**, 43.

[2] Ber. d. chem. Ges. **6**, 711.

Contributions from the Chemical Laboratory of Cornell University.

THE PRODUCTS OF THE CONDENSATION OF ACETONE WITH CONCENTRATED SULPHURIC ACID.[1]

By W. R. Orndorff and S. W. Young.

Historical.

The action of sulphuric acid on acetone was first studied by Sir Robert Kane.[2] He distilled two volumes of acetone with one of concentrated sulphuric acid and obtained, as the principal product of the reaction, a hydrocarbon to which he gave the name mesitylene and for which he deduced the formula C_3H_4 from his analyses. The other products he mentions were mesitic ether and a white waxy substance. These were probably the substances we now know as mesityl oxide and phoron. Kane regarded acetone as an alcohol, and explained the reaction by assuming that acetone, or mesityl alcohol as he called it, formed mesitylene by the loss of one molecule of water, according to the equation

$$C_3H_6O - H_2O = C_3H_4,$$

just as ethyl alcohol yields ethylene under similar conditions.

Hofmann[3] and, later, Cahours,[4] showed that the formula of mesitylene is C_9H_{12}. Hofmann points out that three molecules of acetone condense to one of mesitylene, and calls attention to the resemblance of this reaction to the transition of cyanic acid into cyanuric acid, etc. He continues: "The natural product, too, which we should expect from the dehydration of acetone is a substance of the formula C_3H_4, and it is not improbable that this compound is actually formed at a certain stage of the process; under the influence, however, of the powerful agent in the presence of which it is generated, we find it rapidly converted into a compound containing the triple number of equivalents."

[1] An abstract of this paper was read before the Chemical Section of the American Association for the Advancement of Science at the Rochester meeting.

[2] On a Series of Combinations derived from Pyroacetic Spirit. Graisberry, Dublin, 1838; J. prakt. Chem. (1838) **15**, 129; Ann. der Phys. Pogg. **44**, 473.

[3] Ann. Chem. (Liebig) **71**, 121; Q. J. Chem. Soc. **2**, 104.

[4] Ann. Chem. (Liebig) **74**, 107.

Fittig[1] and his pupils made a thorough study of the reaction between acetone and sulphuric acid, and showed, from its conduct on oxidation, that mesitylene contained three methyl groups. The method of preparation of mesitylene finally adopted by Fittig[2] was as follows: Two volumes of sulphuric acid, previously diluted with one volume of water, are slowly added to a mixture of crude acetone and sand contained in a large retort. The mixture is allowed to stand for twenty-four hours and is then distilled. The crude mesitylene thus obtained is separated from the aqueous layer, washed with a solution of caustic soda and subjected to fractional distillation. By this methed he succeeded in obtaining 100 grams of mesitylene from three pounds of acetone. Fittig states that gases are evolved during the reaction: sulphur dioxide in considerable quantity, and with it a gas which smelled like allylene (methyl acetylene). The reaction expressing the condensation of acetone to mesitylene he writes as follows:

$$3C_3H_6O - 3H_2O = C_9H_{12}.$$

He explains this reaction by assuming that by the action of sulphuric acid on acetone, allylene is first formed according to the equation

$$C_3H_6O - H_2O = C_3H_4,$$

and that this allylene thus formed undergoes polymerization in the presence of the sulphuric acid, resulting in the formation of mesitylene. Mesitylene he considers as triallylene, and thinks that perhaps it may be possible to isolate also a diallylene, C_6H_8, from among the products of the reaction.

Holtmeyer,[3] working with Fittig, showed that mesityl oxide, boiling at 128°–130°, prepared from commercial acetone, when mixed with one-half its volume of strong sulphuric acid, and distilled, after the mixture had been allowed to stand two days, gave two hydrocarbons: mesitylene, boiling at 163°–166°, and another hydrocarbon boiling at 195°. He regards mesityl oxide as an intermediate product between acetone and mesitylene. The product boiling at 195° is more easily obtained, according to Holtmeyer, from the residues obtained in the preparation of mesitylene, especially if one lets the mixture of acetone and sulphuric acid stand for some time before distilling. This hydrocarbon is con-

[1] Ann. Chem. (Liebig) **141**, 129. [2] *Ibid.* **147**, 42.
[3] Ztschr. Chem. 1867, 688.

taminated with sulphur compounds, (mercaptans), from which it is purified by repeated distillation over sodium. When pure it was found to have the composition $C_{10}H_{14}$. With bromine it gave a compound crystallizing from alcohol in needles. This bromine derivative melted between 196° and 202°, and on analysis gave figures corresponding approximately to the formula $C_{10}H_{12}Br_2$. With fuming nitric and sulphuric acids Holtmeyer claims to have obtained a nitro-compound which gave figures on analysis corresponding to the formula $C_{10}H_{11}(NO_2)_2$. The barium salt of the sulphonic acid he states corresponds in the amount of barium to the formula $(C_{10}H_{13}SO_4)_2Ba$. This barium salt was tolerably soluble in water and crystallized in shining needles. Holtmeyer in no case gives the results obtained in his analyses.

Baeyer,[1] in 1866, in a paper On the Condensation Products of Acetone, pointed out that Fittig's work together with his own showed that mesitylene was a trimethylbenzene, and deduced the symmetrical formula for mesitylene, regarding it as benzene in which three methyl groups were symmetrically placed.

O. Jacobsen[2] modified Fittig's method and obtained 110 grams of mesitylene from 1 kilogram of acetone. He found that when large quantities of mesitylene were prepared from acetone and sulphuric acid, he obtained in small quantity a hydrocarbon boiling at about 200°. From the analyses of the barium salt[3] of its sulphonic acid he first thought it was a tetramethylbenzene. He states that Fittig and Bruckner[4] had later obtained a hydrocarbon in the preparation of mesitylene, boiling at 194° to 196°, for which they regard the formula $C_{10}H_{14}$ as probable, and that H. Rose[5] had called attention to the fact that on dissolving crude mesitylene in warm fuming sulphuric acid a sulphonic acid is formed in small quantity which gives a difficultly soluble barium salt, the barium salt of mesitylene-sulphonic acid being quite soluble. Jacobsen then states that if pure acetone be used in the preparation of mesitylene, no higher-boiling products than mesitylene are formed, but that, if the acetone contain higher-boiling products, the mesitylene made from it will contain higher hydrocarbons. His exact words are as follows: "Ich habe bei späteren Darstellungen des Mesitylens widerholt beobachtet, dass bei Anwendung von ganz reinem Aceton keine Spur eines höheren Kohlenwasserstoffes

[1] Ann. Chem. (Liebig) **140**, 297. [2] Ber. d. chem. Ges. **7**, 1432.
[3] Ann. Chem. (Liebig) **146**, 101. [4] *Ibid.* **147**, 44. [5] *Ibid.* **164**, 54.

gebildet wird, dass dagegen, wenn das Aceton höher siedende Verunreinungen enthielt auch das daraus bereitete Mesitylen mit oft nicht unerheblichen Mengen höherer Kohlenwasserstoffe verunreinigt ist." He explains the formation of the hydrocarbons with higher boiling-points by assuming the presence in the acetone used of methylethylketone. Fittig,[1] he states, has already shown that methylethylketone is a constituent of crude acetone, and he himself shows that mixtures of methylethylketone and acetone, when treated with concentrated sulphuric acid and subjected to distillation according to Fittig's method for the preparation of mesitylene, give three hydrocarbons having a higher boiling-point than mesitylene. One of these, boiling at 180° to 184° (corr.), he shows to be 1, 3, 5 dimethylethylbenzene, and the others, boiling at 198° to 200° and 217° to 220°, to be 1, 3, 5 diethylmethylbenzene and 1, 3, 5 triethylbenzene, respectively. He considers the hydrocarbon which he earlier obtained from the crude mesitylene by fractional distillation and which boiled at about 200°, to be identical with the diethylmethylbenzene, obtained from mixtures of acetone and methylethylketone, and not with tetramethylbenzene, as he first stated.[2] The analyses of the barium salt of the sulphonic acid made from this hydrocarbon he states give numbers which agree better with the formula $(C_{11}H_{15}{=}SO_3)_2Ba$ than with the formula $(C_{10}H_{13}SO_3)_2Ba$. The hydrocarbon mentioned by Fittig and Bruckner and, later, by Holtmeyer, which boiled at 194° to 196° and which was obtained from the crude mesitylene, he is inclined to believe is identical with this diethylmethylbenzene.

In an article entitled On the Action of Sulphuric Acid on Allylene,[3] Fittig and Schrohe showed that concentrated sulphuric acid absorbs large quantities of allylene, and that this solution, when diluted with a small quantity of water and subjected to distillation, not only gave mesitylene, but that the solution exhibited on heating all of the properties shown by a mixture of acetone and sulphuric acid when heated, and gave off the same odor. When the solution of allylene in sulphuric acid is diluted with more water than was first used, and the mixture distilled, a considerable quantity of acetone was found in the distillate. These experiments were afterwards repeated[4] with larger quantities of sulphuric acid and allylene, and the earlier observations found to be correct. The

[1] Ann. Chem. (Liebig) **110**, 17. [2] Ber. d. chem. Ges. **7**, 1435.
[3] *Ibid.* **8**, 17. [4] *Ibid.* **8**, 367.

authors are inclined to think that when allylene is absorbed by sulphuric acid there is formed besides the stable allylenesulphonic acid, another very unstable sulphonic acid which is decomposed into acetone and sulphuric acid even on dilution with cold water. From the determination of the amount of barium in the barium salt of the stable sulphonic acid they deduce for it the formula $(C_3H_5SO_3)_2Ba$, which requires 36.53 per cent. of barium, while they found 36.24 per cent. They give neither figures nor weights, do not state whether the barium salt was crystallized or not, and made no other determination than that of barium.

Claisen[1] in 1876 showed that mesitylene was formed directly from acetone by the action of sulphuric acid, and that mesityl oxide and phoron were by-products of the reaction, and not intermediate products. He sums up his results in these words: "Dass der Bildung des Mesitylens aus den Condensationsproductes des Acetons ein Zerfallen derselben in Aceton, resp. in Derivate desselben, vorhergeht. Mesityloxyd und Phoron sind keine Zwischenproducte der Mesitylenbildung. Das neben dem Mesitylen auftretende Mesityloxyd hat nur die Bedeutung eines neben, nicht aber eines Zwischenproductes."

Regarding the way in which the formation of mesitylene from acetone takes place, whether by direct union of three molecules of acetone with loss of three molecules of water, without previous condensation to mesityl oxide or phoron; or by the polymerization of the allylene, which is first formed, as the experiments of Fittig and Schrohe make probable; remains, he says, to be shown.

Bielefeldt,[2] in his inaugural dissertation published in 1880, reviews the various methods for the preparation of mesitylene, and states that he obtained only 100 grams of pure mesitylene from one and a half kilograms of technical or commercial acetone. In order to increase the yield he used pure acetone in the reaction, but found that he obtained no yield of mesitylene at all; though sulphur dioxide, slight traces of mesitylene and water containing acetone distilled, the principal part of the acetone was charred. He says: "Reines Aceton mit Schwefelsäure behandelt gab also fast gar kein Mesitylen; hieraus schloss ich, es sei in dem rohen Aceton ein Körper enthalten aus welchem entweder das Mesitylen entsteht, oder der ganz wesentlich zur Bildung

[1] Ann. Chem. (Liebig) **180**, 22. [2] Ueber Isodurolsulfosäure, etc. Göttingen, 1880.

desselben beiträgt." Since crude acetone contains also methyl alcohol, he supposed that this body might be necessary to form mesitylene, and he tried treating various mixtures of acetone and methyl alcohol with sulphuric acid, but obtained no mesitylene, although he varied the experiments in several ways. By using commercial acetone he succeeded in preparing considerable mesitylene, by Fittig's method, without any further trouble.

W. H. Greene,[1] in 1880, decomposed acetone with zinc chloride at high temperatures and obtained saturated and unsaturated hydrocarbons, (principally propylene), and hexamethylbenzene.

Varenne,[2] in 1883, took up the question of the preparation of mesitylene. He states that Fittig's method gives a very small yield of mesitylene. He therefore first tried the action of chloride of zinc on acetone, but did not obtain any mesitylene. His best results were obtained by mixing 180 grams of acetone and 300 grams of sulphuric acid, and allowing the mixture to stand for one hour. He then distils the mixture, heating it very gently with a rose-burner. When the reaction begins and gas is given off, he passes in steam and lessens the heat or takes the burner away. The distillation in steam is then continued so long as drops of crude mesitylene continue to condense. From the 180 grams of acetone he obtained about 40 grams of crude mesitylene.

Meyer and Jacobson, in their Organic Chemistry (page 411) state on the authority of Bielefeldt in regard to this decomposition of acetone with sulphuric acid, " Es verdient bemerkt zu werden, dass nur aus käuflichem Aceton, nicht aus reinem Aceton durch Condensation mit conc. Schwefelsäure Mesitylen erhalten wird. Welche Beimenge des rohen Acetons für die Mesitylenbildung wesentlich ist, ist nicht aufgeklärt." If this statement be correct, it will be seen that the symmetrical formula for mesitylene, which Baeyer deduces from the condensation of three molecules of acetone to one of mesitylene with the loss of three molecules of water, will not hold, and that our views regarding the relation existing between acetone and mesitylene must be modified.

The following investigation was undertaken to determine, first, whether mesitylene is formed from pure acetone by condensation with sulphuric acid; secondly, if any higher-boiling products than mesitylene are formed when pure acetone is used in the reaction; thirdly, to determine what gases, if any, are given off; and, lastly,

[1] This Journal **2**, 26. [2] Bull. Soc. Chim. (Paris) **40**, 267.

to determine how the reaction, which results in the formation of mesitylene, takes place, *i. e.* whether any intermediate products are formed.

Experimental.

The acetone used in this work was a remarkably pure specimen obtained from the Roessler and Hasslacher Chemical Co., of New York City. The process[1] by which this acetone is made is a patented one and consists in the dry distillation of purified calcium acetate at a low temperature, dry steam being admitted from time to time to regulate the temperature and the process of distillation. The distillate is then treated with milk of lime to remove tarry products and acids, and is then subjected, in the factory, to careful fractional distillation through long rectifying columns arranged on the plan of those used in the rectification of alcohol. A liter of this acetone thus prepared and purified was dehydrated by heating it to its boiling-point for half an hour with fused calcium chloride in a flask connected with a return-condenser. It was then separated from the calcium chloride and distilled. The whole quantity passed over between 55.6° and 56.2° C., the barometer indicating a pressure of 746 mm. The thermometer used was a standardized short Anschütz thermometer, and during the distillation the mercury column was entirely surrounded by the vapor of the boiling liquid. This acetone was shown to be free from dimethylacetal, for it gave no trace of methyl chloride when heated with concentrated hydrochloric acid. Had dimethylacetal been present it would have been decomposed by the hydrochloric acid, and methyl chloride would have been one of the products of the decomposition. That this acetone was free from methylethylketone (which boils at about 78°) may be regarded as certain from a consideration of its boiling-point.

The sulphuric acid used in the reaction was the ordinary colorless commercial concentrated sulphuric acid having a specific gravity of 1.82. Several weeks were spent in preliminary experiments to determine the best method of decomposing acetone with sulphuric acid and the best conditions. The method given by Varenne was followed out exactly in accordance with the conditions and quantities of materials he recommends. The average yield of crude mesitylene obtained by this method was 21.5

[1] Patents (U. S.) 38577, July 11, 1888, and 393079, November, 1888.

grams to 180 grams of the acetone used. Various modifications of Varenne's method were then tried. It was found that the yield of crude mesitylene was much larger when the sulphuric acid was added drop by drop to the acetone from a separating funnel, and the flask containing the acetone was kept cold with ice-water and shaken constantly while the acid was being added, so as to obtain a uniform distribution and action of the acid on the acetone. By these modifications of Varenne's method not only was the yield of crude mesitylene increased, but less tar was formed, and the carbonizing effect of the sulphuric acid on heating was much lessened. If the mixture of sulphuric acid and acetone is to be distilled after standing one hour, as recommended by Varenne, then it was found better not to keep the flask cold during the mixing, and to add the acid to the acetone much more rapidly so as to hasten the reaction by the heat developed. The yield of crude mesitylene is much better, however, when the acid is added more slowly to the cooled acetone, as stated above, and the mixture allowed to stand for twenty-four hours at the temperature of the room. The smaller yield of crude mesitylene obtained when the acetone and acid are rapidly mixed results from the carbonizing action of the sulphuric acid on the acetone on heating, as well as from the evaporation of the acetone by the heat of the reaction. When the mixture of acetone and sulphuric acid has stood for twenty-four hours the odor of acetone disappears entirely. The liquid becomes dark reddish brown in color, thick and oily in consistency, and smells somewhat of mesityl oxide.

The apparatus made use of for the distillations consisted of a two-liter balloon-flask which was connected with a condenser and receiver on one side and on the other with a carbon dioxide generator and a steam-boiler. A thermometer dipping into the mixture of sulphuric acid and acetone serves to indicate the temperature of the reaction. When the gases evolved were to be collected, a tubulated receiver surrounded by a freezing mixture was used, and the gases passing from this were collected over strong caustic potash solution in a gas-holder arranged on the plan of a Schiff's nitrometer, with leveling bulb, mercury trap and exit-tube.

This gas-holder consisted of a liter round-bottom flask, with a long neck, turned bottom up. It was closed with a three-hole

rubber stopper. Through one hole passed a bent delivery-tube which held a small quantity of mercury in the bend to serve as a trap and prevent the running back of the caustic potash solution into the receiver owing to the absorption of carbon dioxide. Through the second hole passed the exit-tube. This was of small bore and reached to the top (bottom) of the flask. Through the third hole passed the tube which connected the flask with the leveling bulb. By raising or lowering this leveling bulb it was possible to increase or diminish the pressure at will. At the end of each distillation the gas collected in this holder was transferred to a larger one fitted up in exactly the same manner and, like it, filled with a strong solution of caustic potash (1 part of commercial caustic potash to 2 parts of distilled water).

Several experiments were made to determine whether the distillation in a current of steam increased the yield of crude mesitylene or not. The average yield of crude mesitylene when steam was used was found to be 33 grams to 180 grams of acetone used, but when steam was not used the yield fell to 21 grams of the crude mesitylene to the same quantity of acetone. It is probable that the steam acts here both mechanically and chemically: mechanically, by volatilizing the oil, and chemically, with the sulphuric acid present, by decomposing any sulphonic acids or ethereal salts of sulphuric acid present in the mixture. Miller[1] states in this connection that by distilling the sulphonic acids of the aromatic hydrocarbons the hydrocarbons are regenerated, and he adds that this decomposition is almost quantitative when the sulphonic acid or its salt is heated with an equal weight of oil of vitriol to 110°–170° and steam is conducted through the mixture.

Many experiments were made to determine the best proportions of sulphuric acid and acetone, but those given by Varenne were found to give uniformly the most satisfactory results.

The method of procedure was as follows: 180 grams of the acetone were placed in a 2-liter balloon-flask, the flask cooled with ice-water, and then 300 grams of concentrated sulphuric acid added gradually from a dropping-funnel, the flask being constantly shaken during the addition of the acid. When all the acid had been added the flask was allowed to stand at the temperature of the room for twenty-four hours. It was then connected with the

[1] J. Chem. Soc. **45**, 148. *Cf.* Friedel and Crafts: Bull. Soc. Chim. (Paris) **42**, 66; and Kelbe: Ber. d. chem. Ges. **19**, 93.

condenser and carbon dioxide generator, and after all the air had been expelled, the receiver was connected with the gas-holder described above. The leveling bulb of this holder was then lowered to diminish the pressure, and the flask containing the mixture of sulphuric acid and acetone was heated slowly and gently on a sand-bath. At 120° C. the reaction begins. Sulphur dioxide is evolved in large quantities, and a gas begins to collect in the gas-holder. The temperature gradually rises even though the source of heat be removed, and finally reaches 140° C. When gas ceases to come off the gas-holder is disconnected from the receiver, and the distillation in steam is continued so long as any oil condenses in the receiver. About 100 cc. of gas collects in the holder, and the amount is about the same for each distillation. The liquid in the receiver consists of a lighter, oily, yellow layer (crude mesitylene) and a heavier, aqueous one, saturated with sulphur dioxide. These layers are separated and put aside until sufficient has been collected for examination. There remains in the distilling-flask an upper layer of a black, tarry substance, which partially solidifies on cooling to a thick mass resembling pitch and a lower layer of spent sulphuric acid. The total amount of acetone decomposed in the manner described above was 6.84 kilograms. This required 12.6 kilograms of sulphuric acid, gave 1.05 kilograms of crude mesitylene and nearly two liters of the aqueous layer. The products to be examined are, then, first, the gas; second, crude mesitylene; third, the tar; fourth, the aqueous layer, and, fifth, the spent acid.

The Gas.—After sulphur dioxide and carbon dioxide had been completely removed, by passing some of the gas into a Hempel pipette filled with caustic potash solution, there remained a colorless gas which had a disagreeable odor (reminding one of the odor of illuminating gas), and which burned with a luminous, smoky flame. This gas was found to be slightly soluble in water, to which it imparted its odor, but much more readily soluble in alcohol. It was at first supposed to be allylene (methylacetylene), more especially since it was quite readily absorbed when allowed to stand for a short time in contact with fuming sulphuric acid in a Hempel sulphuric-acid pipette, and slowly decolorized a solution of bromine in water when left standing in contact with it. It was, therefore, passed through a small bulbed U-tube containing an ammoniacal solution of silver nitrate. But though the gas was

passed back and forth a number of times through this solution no absorption took place and not the slightest trace of a precipitate was formed. The U-tube was then filled with an ammoniacal solution of cuprous chloride, and the gas was passed back and forth through this solution a number of times. No absorption took place and no precipitate was formed. From these results it is obvious that no acetylene hydrocarbons were present. To decide this absolutely the reagent recommended by Béhal[1] for detecting the acetylene hydrocarbons was tried. This consists of a saturated alcoholic solution of silver nitrate. Since the reagent must not be present in excess, a small bulbed U-tube holding about 2 cc. was made and two-thirds filled with the reagent. Some of the gas was passed back and forth through this solution a number of times. About 14 per cent. of the gas taken was absorbed by the alcohol, but not the slightest trace of a precipitate could be observed. As this last reagent will detect the merest trace of the acetylene hydrocarbons, it was concluded that hydrocarbons of the acetylene series must be absent. Thinking it possible that the gas might be allene (dimethylenemethane, $CH_2:C:CH_2$) which does not give a precipitate with ammoniacal solutions of silver nitrate or cuprous chloride, but which does give a precipitate when passed into a solution of mercuric chloride, the gas was passed several times back and forth through an aqueous solution of mercuric chloride contained in the small U-tube. No precipitate was formed, however, and it was hence concluded that allene was not present in the gas. In order to determine whether any volatile sulphur compounds, formed by the decomposition and reduction of the sulphuric acid, were present, about half a liter of the gas was burned from a platinum-tipped burner in a Drehschmidt's apparatus used for estimating sulphur in coal-gas. No sulphuric acid could be detected in the solutions in the absorption-bottles, and hence it was concluded that no sulphur compounds were present in the gas. The absorption of the gas by fuming sulphuric acid and the fact that it decolorized bromine water, though to be sure slowly, seemed to point to the presence of hydrocarbons of the ethylene series. It was noted, however, that the longer the gas remained in contact with the fuming sulphuric acid the more it was absorbed, while if it were simply passed into the sulphuric acid pipette and then back again into the burette the amount

[1] Bull. Soc. Chim. (Paris) 1888, **1**, 335.

absorbed was much less. With bromine-water, too, the gas did not act like an alkylene, for though it decolorized bromine-water, it did so very slowly, and after being in contact with an excess of bromine-water the absorption ceased after a time, though there was much gas left. Explosion-analyses were now made with the gas, using Hempel's explosion-pipette.[1] The results follow:

	I.	II.
Volume of gas taken,	5.9 cc.	6.1 cc.
Volume of gas + oxygen,	29.5	30.0
Volume of gas + oxygen + air,	96.4	96.4
Volume after explosion,	79.3	78.7
Contraction,	17.1	17.7
Volume after absorption with potash,	61.1	59.9
Carbon dioxide,	18.2	18.8
Volume after absorption with phosphorus,	54.4	54.5
Oxygen used,	30.2	31.7
Reduced to unit volume of gas:		
Contraction,	2.89	2.90
Carbon dioxide,	3.08	3.08
Oxygen used,	5.12	5.20

The following table gives the theoretical figures for each of the gases named below:

	Propane.	Propylene.	Allylene.
Contraction,	3.00	2.50	2.00 vols.
Carbon dioxide,	3.00	3.00	3.00
Oxygen used,	5.00	4.50	4.00

It will be seen from this table that the results of the explosion-analyses on the gas agree better with those required for propane than with any of the others. Propane was now made, first by the method of Schorlemmer,[2] by the action of zinc and dilute sulphuric acid on isopropyl iodide, but it was found that the gas made in this way contained a considerable quantity of hydrogen. It was accordingly made from an alcoholic solution of isopropyl iodide by the action of the zinc-copper couple, according to the method of Gladstone and Tribe[3] for methane. The isopropyl iodide used was made from glycerin, according to the directions of Markownikow.[4] It boiled at 89°–90° C. at 740 mm. barometric pressure,

[1] Hempel's Gas Analysis, trans. by Dennis (Macmillan), page 102.
[2] Ann. Chem. (Liebig) **150**, 209. [3] J. Chem. Soc. 1884, 154.
[4] Ann. Chem. (Liebig) **138**, 364.

the mercury column of the short Anschütz thermometer being entirely surrounded by the vapor of the boiling liquid. In order to determine whether it contained any allyl iodide or not, some of the isopropyl iodide in alcoholic solution was shaken up with some mercury and allowed to stand for some time. No trace of the mercury-allyl iodide (HgC_3H_5I) was formed, and hence it was concluded that the isopropyl iodide contained no allyl iodide. The propane made from this isopropyl iodide was a colorless gas, with a disagreeable odor, slightly soluble in water, more readily soluble in alcohol. It burned with a luminous, smoky flame, and in general exhibited the properties of the gas obtained by the action of concentrated sulphuric acid on acetone. Analyses of this gas, using the explosion-pipette of Hempel, gave the following results:

	I.	II.
Volume of gas taken,	4.9 cc.	6.0 cc.
Volume of gas + oxygen,	24.2	23.8
Volume of gas + oxygen + air,	98.9	99.1
Volume of gas after explosion,	83.4	80.6
Contraction,	15.5	18.5
Vol. of gas after absorption with potash,	68.4	62.6
Carbon dioxide,	15.0	18.0
Vol. of gas after absorption with phosphorus,	59.4	60.4
Oxygen used,	25.2	30.4
Reducing to unit volume:		
Contraction,	3.16	3.08
Carbon dioxide,	3.06	3.00
Oxygen used,	5.15	5.11

For pure propane the figures should be: contraction, 3.00; carbon dioxide, 3.00; oxygen used, 5.00.

This propane made from isopropyl iodide was absorbed when passed into fuming sulphuric acid, the amount of absorption depending on the length of time the gas remained in contact with the acid. After allowing the gas to remain in contact with fuming sulphuric acid in a Hempel sulphuric-acid pipette for 15 days, it was found that over 50 per cent. of the gas was absorbed, the sulphuric acid becoming first yellow, and, finally, deep red in color. That propane, a member of the marsh-gas series of hydrocarbons, should be absorbed by fuming sulphuric acid—a reagent that is in general use in gas-analysis to absorb unsaturated hydrocarbons—

seemed very remarkable. The experiment was repeated, however, again and again, and always with the same result. Indeed, the amount of absorption seemed to be limited only by the length of time the gas and sulphuric acid remained in contact. 20 cc. of the gas left in contact with fuming sulphuric acid for two months left only 6 cc. of gas, and the absorption was still going on. Meyer and Jacobson in their Lehrbuch der Organischen Chemie (page 444) state: "Man benutzt daher die rauchende Schwefelsäure in der Gasanalyse—z. B. bei der Analyse des Leuchtgases—um die Alkylene zu absorbiren und durch die infolgedessen eintretende Volumverminderung des Gases den Gehalt an Alkylenen festzustellen. Wasserstoff, *Sumpfgas und seine Homologen*, Kohlenoxyd, etc., werden von der rauchenden Schwefelsäure nicht absorbirt, wohl aber ausser den Alkylenen auch das Acetylen und seine Homologen und die aromatischen Kohlenwasserstoffe (Benzol, etc.)." From the results obtained above with propane it is evident that fuming sulphuric acid cannot be used as an absorbent for the unsaturated hydrocarbons if propane be present. Nowhere in the literature could any statement be found regarding the absorption of propane by fuming sulphuric acid. However, an article by Frankland was found, entitled "The Illuminating Power of Hydrocarbons,"[1] in which the Gladstone and Tribe method for making ethane and propane is described. In this article Frankland states that the propane made by the action of granulated zinc on an alcoholic solution of isopropyl iodide, was found to contain *2 per cent. of gas soluble in fuming sulphuric acid*, even after the gas had been passed through an alcoholic soda solution, bromine and water, a strong solution of caustic soda, and an eprouvette filled with lime. And though he passed the gas again through the same series of reagents, omitting only the alcoholic solution of caustic soda, he states that *the amount of gas soluble in fuming sulphuric acid was not very materially diminished.* Frankland probably passed the gas from the burette into the sulphuric-acid pipette, and then ran it back again at once into the burette. Had he allowed the propane to remain in contact with the fuming sulphuric acid for any length of time, the absorption would have been still greater.[2] In its action towards bromine-water the pro-

[1] J. Chem. Soc. **47** (1885), 235.

[2] An investigation on the absorption of ethane, propane and butane by the various reagents used in gas analysis, is now in progress in this laboratory.

pane made from isopropyl iodide was found to conduct itself in a manner similar to that exhibited by the gas from the action of sulphuric acid on acetone. When passed back and forth through a small bulbed U-tube containing bromine-water, it slowly decolorized the bromine-water. The action on the bromine-water was slower than that of the gas from acetone and sulphuric acid, but in general it was the same. When the gas was passed into a pipette containing bromine-water and the pipette was shaken with the propane, about 30 per cent. absorption took place. Some of this absorption was, however, undoubtedly due to the solvent action of the water on the gas.

From the results of the analyses, as well as from the general agreement of the properties and chemical conduct of the two gases, we must conclude that the gas obtained from the action of sulphuric acid on acetone is propane.

Crude Mesitylene.—This product, which formed the upper layer in the receiver, was obtained in the form of a light yellow, mobile oil saturated with sulphur dioxide. To remove this and any other acids which might be present, the crude mesitylene was shaken with caustic soda solution several times and then washed with water. It was then dried in the usual manner with fused calcium chloride. Thus purified, it still had a disagreeable odor, somewhat like that of the mercaptans. With mercury salts it was found to give the reaction for the mercaptans, and when heated with sodium, the product resulting, on treatment with water, gave the reaction with sodium nitroprusside for sodium sulphide. In order to remove these sulphur compounds, the crude mesitylene, freed from acids and from any soluble compounds by the above treatment, was heated to boiling for several hours with thin slices of metallic sodium, in a round-bottom flask connected with a return-condenser. The crude mesitylene became dark colored, and when the contents of the flask cooled, a dark brown gelatinous mass remained suspended in the liquid. It was found impossible to separate the liquid from this gelatinous mass either by filtration or by decantation, since it clogged the filter-paper and remained suspended in the liquid even after long standing. Working with a small quantity of the material, it was found that by diluting with ether the gelatinous mass subsided quickly and the ethereal solution could then be readily decanted off. Two volumes of absolute ether were accordingly added to the whole of the material and the

two liquids well shaken together for some time. The ethereal solution was decanted off after the gelatinous mass had settled. The material left in the flask was then treated several times with ether to extract all the oil, and these portions were added to the first extract. The ether was then distilled off and the treatment with sodium repeated until it ceased to act on the oil. The oil had now lost its disagreeable odor and had only a pale straw-yellow color. It was subjected to fractional distillation in a distilling-flask having a short column of beads in the neck. This flask was placed in a copper air-bath which was heated by a burner. By means of this air-bath and column of beads the temperature could easily be regulated, and a better separation of the oil into its constituents was hence effected by their use. Fractions were taken off at intervals of ten degrees, beginning with the fraction from 160°–170°. About 60 per cent. of the crude mesitylene came over at this point. This was found to consist almost entirely of mesitylene. After careful refractioning, over half a kilogram of pure mesitylene boiling at 164° at 745 mm. barometric pressure, was obtained from the 1.05 kilograms of crude mesitylene. This corresponds to over 11.5 per cent. of the theoretical yield.

After several weeks spent in fractioning the higher-boiling products from the crude mesitylene, fractions were obtained which boiled constantly at 183°–185° and 195°–197° C. The product boiling at 183°–185° was a light, colorless, mobile liquid with quite a marked aromatic odor. Its specific gravity at 0° compared with water at 4° C. was 0.8865. Combustion analyses of the substance gave the following results:

	I.	II.	III.	Average.
Carbon,	81.40	81.66	81.66	81.57
Hydrogen,	10.86	10.90	10.74	10.83
Oxygen (by difference),	7.74	7.44	7.60	7.60

For the formula $C_{14}H_{22}O$ the results would be: carbon, 81.55; hydrogen, 10.67; oxygen, 7.78. It will be seen from a comparison of these figures with the average of the results obtained on analysis, that the latter correspond closely with the formula $C_{14}H_{22}O$.

The vapor-density was determined according to the method of Victor Meyer. The following are the results:

	I.	II.
Weight of substance taken,	0.1725	0.0938
Air displaced,	23 cc.	11.9 cc.
Temperature,	24.5°	26°
Barometer,	746 mm.	747 mm.

	Found. I.	Found. II.	Calculated for $C_{14}H_{22}O$.
Vapor-density,	6.64	7.05	7.16

The formula of the substance boiling at 183°–185° C. is therefore $C_{14}H_{22}O$. Nothing further could be learned regarding this substance, all of it having been used up in the experiments described.

The product boiling at 195° to 197° C. was a colorless liquid with an odor similar to that of mesitylene, but much more marked. It was insoluble in water, but readily soluble in alcohol and in ether. It remained liquid at a temperature of —40° C., although kept at this temperature for several hours. Its specific gravity at 0° compared with water at 4° C. was found to be 0.8961. About 25 grams of this substance were obtained. Combustion-analyses gave the following results:

I. 0.1421 gram gave 0.4693 gram CO_2 and 0.1382 gram H_2O.

II. 0.2490 gram gave 0.8184 gram CO_2 and 0.2403 gram H_2O.

	Found. I.	Found. II.	Calculated for $C_{10}H_{14}$.
Carbon	90.01	89.63	89.56
Hydrogen	10.80	10.72	10.44

The empirical formula appears therefore to be $C_{10}H_{14}$. This agrees with the statements of Fittig and Holtmeyer. A determination of the vapor-density of the substance by the Victor Meyer method gave the following results:

	I.	II.
Weight of substance taken,	0.1352	0.0986
Air displaced,	23.1 cc.	17.5 cc.
Temperature,	16°	17.5°
Barometer,	736.7 mm.	736.4 mm.

	Found. I.	Found. II.	Calculated for $C_{10}H_{14}$.
Vapor-density,	5.04	4.88	4.64

The bromine product was made by adding directly but cautiously four equivalents of bromine to one of the substance contained in a small flask, the flask being cooled by ice-water. A

very violent reaction took place, fumes of hydrobromic acid were abundantly given off and there remained in the flask a solid white material. This was washed with water to free it from bromine and hydrobromic acid, dried and recrystallized from hot alcohol. It was found rather difficult to get the product to melt sharply. This was probably due to the presence of another bromine product with a higher melting-point. After five or six crystallizations from hot alcohol, crystals were obtained which melted sharply at 198° C.

This bromine substitution-product was difficultly soluble in cold alcohol, more readily in hot, and insoluble in water. It crystallizes from hot alcohol in long, glistening white needles which cling together in the form of a matted mass. A determination of bromine in the substitution-product by the Carius method gave the following results:

0.1136 gram gave 0.1462 gram AgBr.

	Found.	Calculated for $C_{10}H_{12}Br_2$.
Br	54.76	54.79

These results show that the product is a dibrom substitution-product of the hydrocarbon $C_{10}H_{14}$. They are in accord with the statements of Fittig and Holtmeyer. A dinitro derivative was made by adding the hydrocarbon to a mixture of fuming nitric and sulphuric acids. A light yellow solid resulted from this reaction. This was subjected to distillation in steam to remove other products, separated from the water, and after three crystallizations from alcohol was found to melt sharply at 157°. Unfortunately but a very small quantity of this substance was obtained and no analyses could be made of it. The product was of a light yellow color, crystallized from alcohol in fine needles, and sublimed quite readily when heated. It was soluble in hot alcohol, less so in cold, and imparted a marked odor of musk to anything with which it came into contact. This odor was especially noticeable when only a very minute quantity was present. The crystals themselves seemed to possess the odor only to a slight degree. This odor of musk was very tenacious, vessels which contained some of the substance three years ago still retaining the odor.

Of the hydrocarbons known having the formula $C_{10}H_{14}$ none agrees with the hydrocarbon under discussion so well as isodurene, unsymmetrical tetramethylbenzene. The following table shows how closely they agree:

	Isodurene.	Hydrocarbon $C_{10}H_{14}$.
Boiling-point,	195°–197° (corr.)[1]	195°–197° (corr.)
Melting-point of dibrom derivative,	199°[2]	198°
Melting-point of dinitro derivative,	156°	157°

Isodurene does not solidify at —20° C. The hydrocarbon $C_{10}H_{14}$ could not be solidified at —40° C. Some isodurene was then made according to the method of Jacobsen[3] by the action of methyl chloride on mesitylene in the presence of aluminium chloride. This, after careful fractional distillation, was found to agree in all respects with the hydrocarbon $C_{10}H_{14}$ obtained from the crude mesitylene. It had the same boiling-point and specific gravity, the same odor, and yielded with bromine a dibrom-product melting at 198° and with nitric and sulphuric acid a dinitro-product melting at 157°. In order to determine absolutely whether this hydrocarbon $C_{10}H_{14}$ was identical with isodurene or not, both hydrocarbons were oxidized with a solution of potassium permanganate.[4] Both gave mellophanic acid, tetracarboxylbenzene, as the final product of the oxidation.

From these results it was concluded that the hydrocarbon was isodurene, notwithstanding Jacobsen's statements to the contrary. It was also concluded that the nitro-product obtained by Fittig and Holtmeyer from this hydrocarbon was the dinitro-product, and not the trinitro-product as stated by these authors. It will be seen also from the above results that *pure* acetone when decomposed with concentrated sulphuric acid according to the method described, gives 11.5 *per cent. of the theoretical yield of mesitylene, and that higher-boiling products than mesitylene are formed in the reaction.* As these results are not in accord with the statement of Victor Meyer based on Bielefeldt's work, that "mesitylene is not formed from pure acetone, but only from the commercial acetone by condensation with concentrated sulphuric acid," and as they do not agree with Jacobsen's assertion that "if pure acetone be used in the reaction, no higher-boiling products than mesitylene are formed," experiments were undertaken, using chemically pure acetone in the reaction. This acetone was made from the sodium bisulphite compound, and was found to boil constantly at 54.8°–55.2° at 727 mm. barometric pressure, using an Anschütz thermometer, the mercury column being entirely sur-

[1] Jacobsen gives 195° (corr.). [2] Jacobsen (Ber. d. chem. Ges. **15**, 1853) gives 209°.
[3] *Ibid.* **14**, 2629. [4] *Ibid.* **17**, 2517.

rounded by the vapor of the boiling liquid. Over a kilogram of this acetone was decomposed with concentrated sulphuric acid according to the method described above. *The products of the reaction were absolutely identical with those obtained in the first case*, so that it can be positively asserted that the *purest* acetone *does* yield mesitylene when treated with concentrated sulphuric acid and distilled, indeed this method can be recommended as the best known at present for the preparation of mesitylene. It may also be stated that higher-boiling products than mesitylene are formed when the purest acetone is used in the reaction.

Attention should perhaps be called to the fact that Bielefeldt's and Jacobsen's results were obtained by using Fittig's method for the preparation of mesitylene, while the results recorded in this paper were obtained by using a modification of Varenne's method.

The Tar.—The mass remaining in the flask after the distillation in steam was poured out into a porcelain dish and allowed to cool. The spent acid was then poured off, and the black tarry mass remaining was washed several times with water and sodium carbonate solution to remove all the sulphuric acid. It was then washed again with water and dried at 100°. When cold it could easily be broken and handled, and was found to resemble the pitch obtained in the distillation of coal-tar. This tar was then subjected to distillation in an iron retort. The distillate consisted of a brown, thick oil with a disagreeable odor, while the mass left in the retort resembled coke. The distillate was redistilled in a vacuum. It boiled from 100° to 300° at 6 cm. pressure. The distillate was then boiled with sodium for several hours to remove sulphur compounds according to the method given above for the purification of the crude mesitylene; it was then separated from the sodium compounds, redistilled, and again treated with sodium. The oil had now lost its disagreeable odor and gave no reaction for sulphur compounds. The product thus purified was now subjected to fractional distillation, using the apparatus described as used to fractionate the crude mesitylene. The fractions were taken off at intervals of ten degrees from 220° to 290°. The fraction boiling at 270° to 280° was by far the largest of all. The fractions boiling over 220°, obtained from the crude mesitylene and having the corresponding boiling-points, were now added to the proper fractions obtained from the tar, and the combined material was subjected to fractional distillation for several

weeks. A compound boiling at 280°–282° was finally separated. This was quite a viscous liquid, with a yellow color and very little odor. Combustion-analyses gave the following results:

	Found.		Calculated for $(C_3H_4)_5$.
	I.	II.	
Carbon	89.85	89.80	89.99
Hydrogen	10.34	10.44	10.00

From the results it will be seen that the analyses correspond closely with the formula $(C_3H_4)_5$. Several attempts were made to determine the vapor-density of this hydrocarbon by the Victor Meyer method as well as by the Hofmann method, but without success, owing to the fact that the substance was changed in some way even when heated to the boiling-point of aniline. The molecular weight of this hydrocarbon was finally obtained by determining the freezing-point of the solution in benzene, using Beckman's method and apparatus. The following results were obtained:[1]

Weight of solvent used, 12.88 grams.

Weight Substance.	Per cent. Solution.	Depression.	Molecular Weight.
0.2049	1.5908	0.387	201
0.4055	3.1483	0.762	202
0.7644	5.9348	1.399	208
	Required for $(C_3H_4)_5$,		200

The formula $(C_3H_4)_5$ or $C_{15}H_{20}$ therefore represents the composition of the molecule of this hydrocarbon.

With bromine this hydrocarbon formed a bromine substitution-product which was a heavy oil. Owing to the small quantity of this hydrocarbon obtained, further study of it and its derivatives was impossible. The formation of this product, a polymer of allylene, C_3H_4, seems to indicate that allylene is really formed in some stage of the condensation of acetone to mesitylene, as was first conjectured by Hofmann and afterwards by Fittig.

The Aqueous Layer.—This product is the aqueous portion of the distillate collected in the receiver. It smells strongly of sulphur dioxide. When distilled it gave a small quantity of liquid boiling below 100°, but the larger portion boiled constantly at 100°. The fraction boiling below 100° was refractioned, and then the lower-boiling portion treated with potassium

[1] These determinations were kindly made for the authors by Dr. John White, of this laboratory.

carbonate. A volatile liquid was thus separated which boiled at 56°–58° and was identified as acetone. The product boiling at 100° was neutralized with sodium carbonate and distilled. The first portions of the distillate came over quite milky and had a strong peppermint-like odor. The distillate was extracted with ether, and after having been separated from the water and dried over calcium chloride the ether was distilled off. An oil boiling at 130° was obtained which was shown to be mesityl oxide. The solution of sodium salts remaining in the flask was evaporated to dryness on the steam-bath and finally heated in an air-bath to 140° C. The thoroughly dried mass was then treated with ethyl-sulphuric acid (made by mixing 1 part alcohol and 2 parts concentrated sulphuric acid) and distilled. The distillate was separated from the water, washed with soda solution, dried with calcium chloride, and again distilled. It was found to boil constantly at 76° (barometric pressure, 745 mm.) and was identified as ethyl acetate by many reactions. The only volatile organic acid present in the aqueous layer was thus shown to be acetic acid. Had other volatile organic acids been present, a mixture of the ethyl salts of these acids would have been formed, and they could have been separated from each other by fractional distillation. This result agrees with the statement of Plantamour,[1] who says that the "watery liquid formed in the preparation of mesitylene contains sulphurous and acetic acids which may be separated by baryta."

Spent Sulphuric Acid.—This is the liquid which, on cooling, separated out from the tar produced in the formation of mesitylene. The dark liquid was poured into ice-water, with constant stirring to prevent rise of temperature. The resulting liquid was neutralized with precipitated chalk, filtered, the filtrate boiled with bone-black to decolorize it, and then evaporated to dryness on the steam-bath. An unpleasant odor resembling that of the geranium (phoron) was noticeable during the boiling of the filtrate with bone-black. A very small residue of a calcium salt which solidified in warty concretions, and which was probably a calcium sulphonate, was left after the evaporation to dryness. It is evident from the very small amount of salt formed in this experiment that all sulphonic acids and ethereal salts of sulphuric acid which might have been formed are decomposed by the subsequent heating with sulphuric acid and distillation in steam.

[1] Gmelin's Handbook of Chemistry, Watts' translation, Vol. IX, p. 9.

Summary.

The results of this work on the products of the condensation of pure acetone with concentrated sulphuric acid may be briefly summed up as follows:

1. Mesitylene is formed in largest quantity, over 11.5 per cent. of the theoretical yield having been obtained. The method can therefore be recommended as the best we have at present for the preparation of this hydrocarbon.

2. A not inconsiderable quantity of the hydrocarbon isodurene (unsymmetrical tetramethylbenzene) is formed at the same time with the mesitylene.

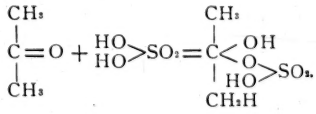
3. A compound boiling at 185° to 187° and having the formula $C_{14}H_{22}O$ is a constant product of this reaction.

4. A hydrocarbon boiling at 280°–282° and having the formula $(C_3H_4)_6$ can be isolated from the tarry products.

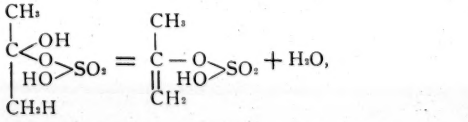
5. Propane is formed in small quantity in this reaction.

6. Besides the five products above-named, sulphur dioxide, acetic acid, mesityl oxide, phoron and sulphur compounds are produced.

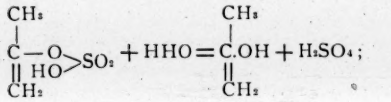
Regarding the method by which mesitylene is formed from acetone, the authors are of the opinion that the acetone first unites with the sulphuric acid, forming an addition-product exactly as it does with hydrocyanic acid. This union of the acetone and sulphuric acid may be represented as follows:



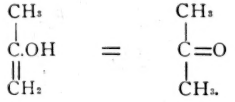
This addition-product then loses water,



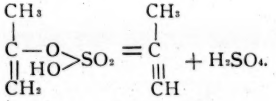
yielding the acid sulphate of isopropenyl alcohol, $CH_3C(OH)=CH_2$. This isopropenyl sulphuric acid with water yields isopropenyl alcohol and sulphuric acid thus:



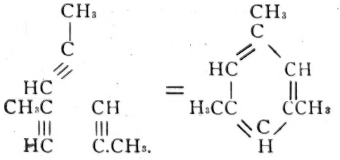
the isopropenyl alcohol forming at once acetone, as it is unstable in the free condition,



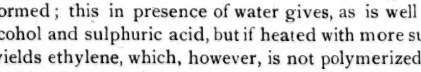
Heated with concentrated sulphuric acid, isopropenyl acid sulphate would yield allylene and sulphuric acid thus:



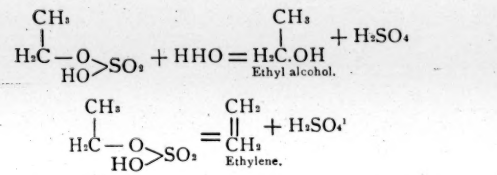
Three molecules of this allylene would then condense in the presence of the strong sulphuric acid and mesitylene would result:



The formation of mesitylene, then, from acetone resembles very closely that of ethylene from ethyl alcohol by the action of sulphuric acid. In the case of the ethyl alcohol, ethyl-sulphuric acid is first formed; this in presence of water gives, as is well known, ethyl alcohol and sulphuric acid, but if heated with more sulphuric acid it yields ethylene, which, however, is not polymerized by sulphuric acid. The equations representing these reactions are as follows:



Ethyl sulphuric acid.

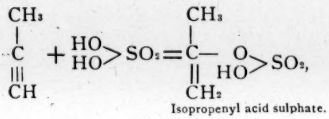


In support of this view of the formation of mesitylene from acetone, it may be said that when acetone and sulphuric acid are mixed, so much heat is evolved that it is necessary to cool with ice-water the flask in which the two liquids are mixed. The mixture is thick and oily, and has lost the odor of acetone entirely. If this mixture of acetone and sulphuric acid (30 grams acetone to 50 of acid) be treated with a liter of water and distilled, almost all the acetone used may be recovered. The product formed by the action of sulphuric acid on acetone, and which the authors believe to be isopropenyl-sulphuric acid, is then decomposed very readily by water into acetone and sulphuric acid. Many attempts were made to prepare salts of this acid, but all failed owing to the fact that in the presence of water the acid decomposes into its constituents.

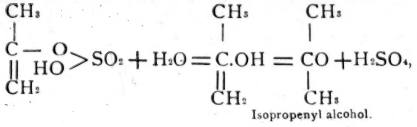
Both Kane[2] and Hlasiwetz[3] claim to have made salts of the acid obtained by the action of sulphuric acid on acetone. They both speak of the instability of this acid and say that it could only be investigated in its salts. Analyses of the calcium salt of this acid are given by Kane and also by Hlasiwetz, but as the acetone used by them was impure and the calcium salt itself was not purified by recrystallization, the analyses are practically of no value. Kane gives to the acid the formula $C_3H_5HSO_4$, while Hlasiwetz claims that it is to be represented by the formula $C_3H_5HSO_5$. The analyses of the calcium salt do not agree very well with each other nor with either formula.

It is very probable that this same isopropenyl acid sulphate is formed when allylene dissolves in concentrated sulphuric acid. Fittig found that if this solution be diluted with water and distilled, acetone is formed, while if it be diluted with but little water and distilled, mesitylene results. These reactions may be represented as follows:

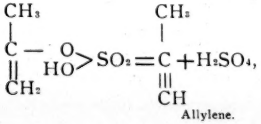
[1] Meyer and Jacobson: Organ. Chemie **1**, 438.
[2] J. prakt. Chem. **15**, 144. Ann. der Phys. Pogg. **44**, 179. [3] *Ibid.* **69**, 369.



Isopropenyl acid sulphate.

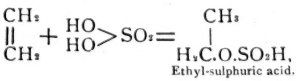


Isopropenyl alcohol.

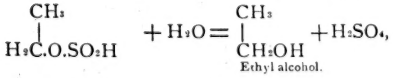


Allylene.

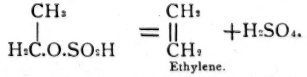
three molecules of the allylene thus formed uniting at once and yielding mesitylene. The reactions represented above are strictly analogous to the reactions by which ethylene is converted into alcohol and back again into ethylene: ethyl-sulphuric acid is first formed, and this with water yields ethyl alcohol and sulphuric acid, but when heated with sulphuric acid it gives ethylene and sulphuric acid, thus:



Ethyl-sulphuric acid.



Ethyl alcohol.



Ethylene.

The polymerization of the unsaturated hydrocarbons by sulphuric acid is well known: thus, isobutylene, C_4H_8, forms a di- and tri-isobutylene. According to Butlerow,[1] an addition-product is first formed, thus:

$$(CH_3)_2.C=CH_2 + H_2SO_4 = (CH_3)_2.C<\begin{matrix}CH_3\\SO_4H\end{matrix}.$$

[1] Ann. Chem. (Liebig) **189**, 65.

This with a second molecule of isobutylene condenses to diisobutylene, sulphuric acid splitting off, thus:

$$(CH_3)_2.C:CH_2+HSO_4.C.(CH_3)_3=(CH_3)_2C:CH.(CH_3)_3+H_2SO_4$$

The diisobutylene thus formed then unites with another molecule of the sulphuric-acid addition-product of isobutylene, forming triisobutylene and sulphuric acid.

It is quite likely that the polymerization of allylene by sulphuric acid takes place in a similar manner, an addition-product, isopropenyl acid sulphate, being first formed. This would then unite with another molecule of allylene to form diallylene, sulphuric acid being eliminated, and the diallylene would in the same way form triallylene or mesitylene by uniting with a molecule of isopropenyl acid sulphate. The formation of the product boiling at 280°–282°, having the formula $(C_3H_4)_3$, and which may be called pentallylene, indicates that this view is not altogether improbable.

Acetylene is slowly absorbed by concentrated sulphuric acid, and, if the solution thus formed be distilled with water, acetic and crotonic aldehydes are formed.[1] According to Zeisel,[2] a sulphonic acid is formed here; but it is quite probable that the reaction is similar to that which takes place when allylene is absorbed by sulphuric acid; vinyl acid sulphate is probably first formed by direct addition of the acetylene and sulphuric acid, according to the equation:

$$\begin{matrix} CH \\ \| \\ CH \end{matrix} + \begin{matrix} HO \\ HO \end{matrix}\!\!>\!SO_2 = \begin{matrix} CH_2 \\ \| \\ HC\!-\!O \\ HO \end{matrix}\!\!>\!SO_2.$$

Vinyl acid sulphate.

This vinyl acid sulphate with water would then on distillation yield vinyl alcohol and sulphuric acid, the vinyl alcohol at once forming aldehyde, thus:

$$\begin{matrix} CH_2 \\ \| \\ HC\!-\!O \\ HO \end{matrix}\!\!>\!SO_2 + H_2O = \underset{\text{Vinyl alcohol.}}{\begin{matrix} CH_2 \\ \| \\ HC.OH \end{matrix}} = \underset{\text{Aldehyde.}}{\begin{matrix} CH_3 \\ | \\ HC=O \end{matrix}} + H_2SO_4;$$

the crotonic aldehyde resulting from the further action of the sulphuric acid on the aldehyde. Vinyl alcohol and its derivatives have been known for some time, but isopropenyl alcohol is not

[1] Ber. d. chem. Ges. **10**, 637. [2] Ann. Chem. (Liebig) **191**, 372.

known in the free state: it at once yields acetone.[1] It is, however, known in the form of the ethyl ether,[2] which is formed by heating allylene with alcoholic potash to 170°–180°. The reaction is represented thus:

$$CH_3C \equiv CH + HOC_2H_5 = CH_3.C(OC_2H_5) : CH_2.$$

This ether is very readily decomposed by dilute sulphuric acid into acetone and ethyl alcohol.

Concerning the formation of the other products of the reaction between acetone and sulphuric acid nothing further was learned.

The authors of this paper wish to express their thanks to Mr. E. M. Chamot of this University for the analyses of the gas formed in the reaction, as well as of the propane.

CORNELL UNIVERSITY, *January*, 1893.

PENTOSANS IN PLANTS.

BY G. DE CHALMOT.

Continuing my work[3] of last summer, I investigated the conduct of the pentosans by the germination of seeds. The methods which I used for the detection and quantitative analysis of the pentosans in their different forms are the following:

1st. For the determination of total pentosans I use in principle the method of Tollens and myself. I follow the additional hints given by Flint,[4] making some alterations on account of the small amount of pentosans contained in seeds. I proceed as follows: I distil very slowly (10 cc. in 20 minutes), adding every 20 minutes 10 cc. of hydrochloric acid All the furfurol will be found in the first 100 or 110 cc. of the distillate. After neutralizing as usual, I bring the volume of the liquid to 200 cc. by adding a 19.3 per cent. sodium chloride solution. After precipitating the furfurol I stir for half an hour, following the directions of Flint. As Flint[5] found that furfurol-hydrazon is nearly insoluble in a stronger solution of sodium chloride, I neglect the small amounts which remain

[1] Meyer and Jacobson: Org. Chem. **1**, 475. [2] Ber. d. chem. Ges. **21c**, 614.
[3] See this Journal **15**, 21. [4] Inaug. Diss. (Göttingen) 1892. [5] *l. c.* p. 20.

in the solution. I further assume that the pentosans yield 50 per cent. of furfurol, which figure renders the calculation easy. When working as described, I got nearly as good results as those obtained by Flint, and found the method more practical if only small amounts of pentosan are present. It requires, though, much watching, as the results can vary greatly if the time of the distillation is not kept within the limits. When larger amounts of pentosans are present, the old way of working seems to me preferable.

2d. For the determination of the pentosans which are insoluble in dilute acids (cellulose-pentosans), I heat 10 grams of substance with 200 cc. of hydrochloric acid (of 1.25 per cent. HCl). I heat the insoluble residue three times more with water, place it on a filter, dry it and distil it with 100 cc. of hydrochloric acid (of 12 per cent. HCl).

3d. To detect the small amounts of soluble pentosans I determine the total amount of carbohydrates and the amount of furfurol obtained by distillation with hydrochloric acid, as described in my former paper.

Last summer I assumed that the largest amount of furfurol which hexoses can yield is 0.2 per cent. As I based this presumption on analyses made with small amounts of cane sugar only, it seemed to me not superfluous to repeat those analyses, taking larger amounts of cane sugar and of sugar of milk.[1] For these determinations I used the colorimetric method.

Cane sugar recrystallized out of dilute alcohol in large crystals: (1.) 5 grams substance taken. The strength of the furfurol solution was +0.5 cc., therefore the sugar yielded 0.125 per cent. of furfurol. (2.) 5 grams substance, +(0.5–1) cc. or 0.1375 per cent. of furfurol. Average of two analyses is 0.13 per cent. of furfurol. The percentage obtained with 0.5 gram of cane sugar last summer was 0.04–0.2 per cent. of furfurol.

Sugar of milk recrystallized out of water: (1.) 5 grams substance, —(2.5–3) cc. or 0.042 per cent. of furfurol. (2.) 5 grams substance, —(2–2.5) cc. or 0.047 per cent. of furfurol. Average of two analyses is 0.045 per cent. of furfurol.

Allowing that glucose and galactose yield the same percentage of furfurol, and considering that 5 grams of sugar of milk yield

[1] With regard to the presence of galactans in seeds see Schulze, Steiger and Maxwell: Landw. Vers. St. **39**, 269–329.

2.63 grams of glucose and 2.63 grams of galactose, glucose and galactose each yield 0.043 per cent. of furfurol. Cane sugar yields equal amounts of glucose and of fructose. The percentage of furfurol yielded by fructose can now be calculated, being 2(0.13 × 0.95)—0.043 or nearly 0.2 per cent. The figure 0.2 per cent. for the largest possible amount of furfurol which hexoses can yield, is therefore well chosen.

In all the seeds which I tested I found water-soluble methylpentosans which yield methylfurfurol. I had therefore to detect furfurol in a solution in which also methylfurfurol was present. I will communicate in a few words an account of the reactions which proved efficient for the detection of furfurol and of methylfurfurol when present at the same time in an acetic acid solution.[1]

Furfurol, aniline and acetic acid yield a red dye, an acetate of furfur-aniline. Methylfurfurol, aniline and acetic acid yield a yellow dye, probably an acetate of methylfurfur-aniline. The chloride, nitrate and sulphate of furfur-aniline are red.[2] The same salts of methylfurfur-aniline are also red. Furfur-aniline salts cannot be formed unless there is less mineral acid present than is equivalent to the amount of aniline in the solution. The limits in the case of the formation of methylfurfur-aniline salts are the same. Furfur-aniline salts are very unstable. Methylfurfur-aniline salts are much more stable. If small amounts of methylfurfurol are to be detected in the presence of large quantities of furfurol, I treat the acetic acid solution with my aniline reagent (1 per cent. aniline in 95 per cent. alcohol). The dyestuffs are readily formed, but the yellow color is not visible on account of the red being prevalent. I allow the solution to stand exposed to the light until the red color has vanished (one or more days). I add then a drop of hydrochloric acid. If a reddish tinge appears and remains, even after several hours, methylfurfurol has been present. The appearing of a reddish color does not directly prove that methylfurfurol is present, as the chloride of furfur-aniline is a much stronger dye than the acetate is. It is, therefore, possible for the amounts of acetate to be so small as to be invisible. When they are converted into the chloride they become visible, but vanish very soon. To

[1] The reaction of Maquenne (Compt. Rend. **109**, 571) cannot be used to ascertain the presence of methylfurfurol, when this is strongly diluted.

[2] Hill (Ber. d. chem. Ges. **22**, 607) and Bieler (Inaug. Diss. [Göttingen, 1890] pp. 24) state that methylfurfurol treated with aniline and acetic acid, yields a yellow dye, which gradually changes into orange red, though they do not give an explanation of this change.

use this reaction with perfect certainty requires some experience. To detect small amounts of furfurol in the presence of larger quantities of methylfurfurol is more difficult. The color obtained after adding aniline is yellow, and the red tinge is not visible. If the amount of furfurol present is not too small, it can be made evident by adding to the solution a drop of aniline oil. If this be carefully done the drop sinks to the bottom of the tube, without mixing much with the acid liquid. If furfurol is present a reddish hue can be observed directly above the aniline.[1]

The experiments were made with peas and with corn. Analyses were made of the seeds before germination, and of the different parts of the young plants after germination in darkness. I allowed the seeds to swell in water and then put them into soil. The soil used contained small amounts of pentosans and methyl-pentosans. The roots of the young plants were therefore carefully washed. The matter used for analysis was always finely pulverized and thoroughly mixed. Further details can easily be learned from the figures given below.

TABLE I.—PEAS (*Pisum sativum* L.).

A sample of selected peas weighing each 0.260 gram (0.255–0.265) was used.

a.—Before the Germination.

77 peas = 19.0380 grams of dry matter. 1 pea = 0.2474 gram of dry matter.

4.7190 grams of dry matter yielded 0.1784 gram of hydrazon = 3.90 per cent. of total pentosan; 4.5392 grams of dry matter yielded 0.1639 gram of hydrazon = 3.72 per cent. of total pentosan; average = 3.81 per cent. of total pentosan.

9.0740 grams of dry matter yielded, after treatment with acid, 0.0778 gram of hydrazon = 0.88 per cent. of cellulose-pentosan.

b.—After the Germination from 19 *November to* 6 *December.*

The average length of the main roots was 12.8 cm., and of the stems 21.4 cm.

[1] It may be that there are two acetates of furfur-aniline. The one which is formed in the acetic acid solution might be a diacetate. Aniline acting upon this compound might possibly form a monoacetate and aniline hydrochloride. The monoacetate should be a stronger dye than the diacetate. If to a solution of furfur-aniline in acetic acid an excess of aniline is added, the color gets noticeably darker. The study of the acetates is much hindered by reason of their tendency to decompose.

100 plants = 20.40 grams of dry matter. 1 plant = 0.2040 gram of dry matter.

Analyses of plants: 4.8184 grams of dry matter yielded 0.2572 gram of hydrazon = 5.52 per cent. of total pentosan; 4.8146 grams of dry matter yielded 0.2388 gram of hydrazon = 5.12 per cent. of total pentosan; average = 5.32 per cent. of total pentosan.

9.6330 grams of dry matter yielded, after treatment with acid, 0.1262 gram of hydrazon = 1.38 per cent. of cellulose-pentosan.

90 stems = 4.881 grams of dry matter yielded 0.2474 gram of hydrazon. 1 stem contained 0.0028 gram of total pentosan.

90 roots = 3.2970 grams of dry matter yielded 0.1291 gram of hydrazon; 1 root contained 0.0015 gram of total pentosan.

Before the Germination. Gram.	After the Germination. Gram.	Gain or Loss. Gram.
1 seed = .2474 dry matter.	1 plant = .2040 dry matter.	—.0434
1 " = .0094 total pentosan.	1 " = .0109 total pentosan.	+.0015
1 " = .0022 cellulose-pentosan.	1 " = .0028 cellulose-pentosan.	+.0006
	1 stem = .0028 total pentosan.	
	1 root = .0015 " "	
1 " = .0094 total pentosan.	1 seed (by calculation) = .0066 total pentosan.	—.0028

TABLE II.—CORN (*Zea Mays* L.).

A sample of selected corn was thoroughtly mixed. Of each 5 specimens, 4 were taken for germinating and 1 for analysis.[1]

Average weight of 1 seed for germinating = 0.4776 gram; average weight of 1 seed for analysis = 0.4858 gram.

a.—Before the Germination.

4.7706 grams (10 seeds) = 3.9188 grams of dry matter = 82.14 per cent. 1 average seed of 0.4776 gram contained 0.3923 gram of dry matter.

4.2256 grams of dry matter yielded 0.1914 gram of hydrazon = 4.68 per cent. of total pentosan; 4.0946 grams of dry matter yielded 0.1854 gram of hydrazon = 4.62 per cent. of total pentosan; average = 4.65 per cent. of total pentosan.

[1] I could not get a sample of corn from which each seed had nearly the same weight, as was the case with the peas. The weight of the seeds varied a great deal.

8.4511 grams of dry matter yielded, after treatment with acid, 0.0075 gram of hydrazon = 0.09 per cent. of cellulose-pentosan.

b.—After the Germination from 5–26 December.

The average length of the stems was 20 cm.

	Grams.		Gram.
344 seeds	= 83.6 dry matter, 1 seed	=	0.2430
344 stems and roots	= 41.8 dry matter, 1 stem and root	=	0.1215
		1 plant =	0.3645

Analyses of seeds: 4.8335 grams of dry matter yielded 0.2800 gram of hydrazon = 5.98 per cent. of total pentosan; 4.7718 grams of dry matter yielded 0.2685 gram of hydrazon = 5.80 per cent. of total pentosan; average = 5.89 per cent. of total pentosan.

Analyses of stems and roots: 4.8671 grams of dry matter yielded 0.2871 gram of hydrazon = 6.08 per cent. of total pentosan; 4.8700 grams of dry matter yielded 0.2720 gram of hydrazon = 5.76 per cent. of total pentosan; average = 5.92 per cent. of total pentosan.

Before the Germination. Gram.	After the Germination. Gram.	Gain or Loss. Gram.
1 seed = .3923 dry matter.	1 plant = .3645 dry matter.	—.0278
1 " = .0182 total pentosan.	1 seed = .0143 total pentosan.	—.0039
1 " = .0004 cellulose-pentosan.	1 stem + root = .0072 total pentosan.	
1 " = .0182 total pentosan.	1 plant (by calculation) = .0215 total pentosan.	+.0033

The results are chiefly the following: First, the pentosans decrease in the seeds during the germination, and appear again in the stems and roots; they are therefore transferred. Second, the total amount of pentosans increases during the germination.

The amount of cellulose-pentosans also increases, but the difference in the figures obtained from peas is too slight to produce an absolute certainty in this respect.

The amount of cellulose-pentosans in corn being very small, I did not determine it after the germination.

With regard to the first result, it was desirable to trace the soluble pentosans which ought to be present when pentosans are transferred.

When I prepared an extract of the young plants by immersing them in water in the same way as I formerly treated green leaves, I could not trace pentosans in the solution, but methyl-pentosans very distinctly. This tempted me to believe that only methyl-pentosans were transferred. This being the case, there should be a difference in the melting-points of the hydrazons obtained from seeds before and after germination, as furfurol-hydrazon melts at 98° C., and methylfurfurol-hydrazon is still a liquid at 15° C.[1] In order to test this I dried the hydrazons obtained by four different distillations of corn, in a desiccator, and determined their melting-points. The melting-point of hydrazon from seeds before germination was found to be 87°–88° C., and of hydrazon from seeds belonging to plants of 4 weeks old was found to be 88°–89° C. As the melting-points were nearly the same, the constitution of the hydrazons obtained from seeds before and after germination was also not very different, and the relation between the amounts of pentosans and methyl-pentosans in the seeds was in both cases the same or nearly the same.

I tried once more to trace soluble pentosans, using the pressed-out juice of the young plants, and was successful. In the juice of germinated peas, smaller amounts of methyl-pentosans are contained than in the extract obtained by immersing the germs for a longer time in water.

The juice is much more concentrated than the extract, and on this account the percentage of pentosans in it is larger. The juice from peas of 3½ weeks old yielded a red color with aniline. The color was too brown (presence of methylfurfurol) to be accurately compared with the standard furfurol solution, but there was surely more than 0.00005 gram of furfurol in 1 cc. liquid. The original liquid contained 0.5 per cent. of hexoses, and therefore the hexoses present could not have yielded more than 0.00001 gram of furfurol in 1 cc., and probably they yielded much less.

In a somewhat diluted juice from corn-germs there was still a large amount of methyl-pentosans present. I could distinctly trace furfurol when adding aniline oil as described above. I could not prove that the furfurol was more than what the hexoses (2 per

[1] E. Fischer: Ber. d. chem. Ges. **17**, 574; Hill, *l. c.*

cent.) could yield, but I have no doubt of it, as the amount of furfurol that the hexoses have yielded was probably much less than 0.00004 per cent., and it would not be possible to trace this small amount.

Juice from *Tropæolum* yielded more than 0.0001 per cent. of furfurol. I did not determine the amount of hexoses on account of the small quantity of juice. It was evident, though, that they did not yield so much furfurol.

The fact that pentosans insoluble in water are dissolved in the seeds and transported during the germination is of the highest importance, touching the theory of the formation of pentosans by the assimilating process. I have pointed out in my former article that it is probable that pentosans which are formed by the assimilating process are temporarily precipitated and dissolved when the main assimilation is over.

I have proved now that pentosans when once precipitated can be dissolved and transported again, which gives to the hypothesis a firmer foundation than I was able to give it before.

When discussing this hypothesis I mentioned that it seemed not improbable to me that under the circumstances by which aldehydes can form the polymeric sugars, the reverse could also take place. I was then not acquainted with a recent publication of J. Traeger,[1] who has proved that paraldehyde forms aldehyde again under probably the same circumstances that aldehyde can form paraldehyde. I am gratified that this fact in some degree supports my suggestion.

I found that during the germination the amount of pentosans increases. This result might be due to two different causes: First, the pentosans might be formed out of other substances; second, the pentosans might be absorbed out of the soil in which pentosans are present. In order to know which of these two causes was the true one I allowed peas to germinate into asbestos in which no pentosans are present.

TABLE III.

40 peas for germinating weighed 8.55 grams, or 1 pea = 0.2137 gram.

The sample contained 92.92 per cent. of dry matter, therefore 1 pea before the germination = 0.1986 gram of dry matter.

[1] Ber. d. chem. Ges. 25, 3316.

For analysis, 100 peas = 21.40 grams were used, or 1 pea = 0.2140 gram.

4.5218 grams of dry matter yielded 0.1854 gram of hydrazon = 4.24 per cent. of pentosan; 4.5218 grams of dry matter yielded 0.1886 gram of hydrazon = 4.30 per cent. of pentosan; average = 4.27 per cent. of pentosan.

After germinating from 3–27 of January, the 40 peas weighed when dried 7.910 grams, which included some asbestos that could not be easily removed. A determination of ash showed 35.5 per cent. of it; therefore more than 5 grams had to be used for the determination of pentosan.[1]

6.716 grams of dry matter yielded 0.2908 gram of hydrazon = 4.46 per cent. of pentosan.

Before the Germination.	After the Germination.
1 seed = 0.0085 gram of pentosan.	1 plant = 0.0088 gram of pentosan.

No material gain in pentosans was obtained, and it seems therefore probable that the germs can absorb pentosans out of the soil.

I hope to investigate this matter more thoroughly. Some seeds contain large amounts of pentosans,[2] and it seemed to me not superfluous to examine if also in these seeds the amount of pentosans does not diminish during the germination.

For this examination I used the seeds of *Tropæolum majus*. As the dried-up fruits could not easily be removed, I allowed the seeds to lie in water for some days, after which treatment the fruits could be easily taken away. The germination took place in earth.

TABLE IV.

209 seeds for germinating = 41.19 grams. 1 seed = 0.1970 gram.

151 seeds for analysis = 29.25 grams. 1 seed = 0.1937 gram.

a.—Before the Germination.

151 seeds or 29.25 grams contained 13.0808 grams of dry matter = 44.72 per cent.

1 average seed of 0.1970 gram contained 0.0881 gram of dry matter.

3.9606 grams of dry matter yielded 0.4629 gram of hydrazon

[1] Flint: *l. c.*

[2] Ber. d. chem. Ges. **25**, 1238.

= 12.08 per cent. of pentosan; 3.9606 grams of dry matter yielded 0.4547 gram of hydrazon = 11.86 per cent. of pentosan; average = 11.97 per cent. of pentosan.

b.—After the Germination from 1–15 January.

207 plants = 16.61 grams of dry matter. 1 plant = 0.0802 gram. 3.9275 grams of dry matter yielded 0.2289 gram of hydrazon = 6.02 per cent. of pentosan.

Before the Germination. Gram.	After the Germination. Gram.	Loss. Gram.
1 seed = 0.0105 pentosan.	1 plant = 0.0050 pentosan.	—0.0055

These results are striking. The pentosans have diminished by more than one-half.

It remains to be examined whether there are other seeds in which the pentosans decrease so strongly during the germination, and whether the pentosans in *Tropæolum* are the same as those in corn and peas. I hope to be able to furnish a communication on these matters hereafter.

RICHMOND, VA., *February*, 1893.

Contributions from the Chemical Laboratory of the U. S. Department of Agriculture.

XXIII.—SOME PRODUCTS OF CASSAVA.[1]

BY E. E. EWELL AND H. W. WILEY.

Some four years ago one of us[2] described a plant which has been grown in Florida for many years under the name of sweet cassava, the botanical name of which is *Jatropha manihot* or Aipi. From the analyses made at that time it was found that the plant was valuable for feeding purposes, being very rich in carbohydrates although rather poor in albuminoids. Lately the subject has been studied to a much greater extent with the object of preparing as large a number of products as possible from the plant, with the determination of their chemical properties and food values.

[1] Read before the Washington Chemical Society, February 9, 1893.
[2] Wiley: Agric. Science, Vol. 2, No. 10, pp. 256 *et seq.*

A large quantity of the root was obtained from Florida, the bark separated from the root and each subjected to analysis with the following results:

	Peeled root.		Fiber after removal of starch.	Bark of root.	
	Fresh.	Dry.	Dry.	Fresh.	Dry.
Moisture,	61.30	...	..	61.30	..
Ether extract,	0.17	0.44	0.30	0.66	1.70
Albuminoids (nitrogen × 6.35),	0.64	1.66	1.02	2.29	5.91
Starch (diastase extract inverted with HCl),	30.98	80.06	64 64	..	..
Fiber,	0 88	2.26	10.68	3.83	9 89
Ash,	0.51	1.31	1.42	2.02	5.23
Undetermined,	5.52	14.27	21.94	29.90	77.27
	100.00	100.00	100.00	100.00	100.00

With the starch in the analysis given above is reckoned also the soluble carbohydrates, consisting almost exclusively of cane sugar, and of which, in an analysis of another portion of the dry substance, as high as 17 per cent. was found. The undetermined portion consists of the digestible fiber and carbohydrates of the pentose series. The pentosans in the fiber were determined by the furfurol process, as modified by Krug, and the amount in the air-dried material was found to be 3.92 per cent., and in the material after the removal of the starch, 5.33 per cent.

The fresh root was found to contain 38.7 per cent. of dry matter, being considerably more than was found in the fresh sample of the previous analysis. Of this 38.7 per cent., 30.98 consisted of starch and soluble carbohydrates.

Experiments were made to determine the yield of air-dry starch which could be obtained from the roots by laboratory work. Two sets of experiments were made. In the first set the roots were pulped on a Pellet rasp used for preparing beet pulp for instantaneous diffusion. 12 kilos of the unpeeled root were rasped in this way and the starch separated by washing through a sieve of bolting cloth. The washings and settlings were collected and dried in the ordinary method of starch manufacture. The yield of pure starch was 3105 grams, equivalent to 25.9 per cent. of the total weight of the root. The starch was almost absolutely pure, containing only a trace of nitrogenous matter. In the second experiments 10 kilos of the root were ground in a pulping machine

used for preparing green fodder for analysis. The pulp was much less fine than that produced by the Pellet rasp. Treated in the same way, the yield of air-dry starch was 2360 grams or 23.6 per cent. One of the striking points in connection with the work is that the residue from the starch, which consisted largely of fiber, as will be seen by reference to the above analysis, contained still a large percentage of starch, showing that by the process employed the whole of the starch was not secured from the pulp. The diameter of the starch granules is a little over .01 mm., being about seven times smaller than the average of potato starch.

The cassava which grows in tropical regions contains a notable percentage of hydrocyanic acid, so great, in fact, that it cannot be used directly as a food. The so-called poisonous cassava is boiled to expel the hydrocyanic acid before being used for feeding purposes. A careful determination was made of the hydrocyanic acid in the fresh root and the amount was found to be .015 per cent. While this shows a considerable quantity of hydrocyanic acid, it is hardly in proportions sufficiently large to be alarming. Nevertheless, any possible danger could be avoided before using the material as a food, by subjecting it to a sufficient heat to expel the hydrocyanic acid. The hydrocyanic acid seems to be distributed throughout the pulp, and particularly in the juices which can be expressed from the pulp. No injurious effect from the hydrocyanic acid has ever been observed in the case of animals fed on cassava in Florida.

The bark of the root was also subjected to analysis, as will be seen by reference to the above table. It contained no starch, the undetermined matter being chiefly digestible fiber and pentosans.

The mineral matters extracted from the soil are distributed as indicated in the table. The amount of ash in the root itself is quite low, showing that the cassava plant does not require a soil very rich in mineral constituents. The amount of mineral matter taken from the soil by 100 kilos of the fresh root is approximately only half a kilo. The albuminous matters are also present in small quantities, being only slightly larger in weight than the ash itself. The plant, therefore, is one which seems particularly suited to feed almost exclusively from the air and water, and hence is one which could be recommended on the sandy soils of Florida as a crop which would require the minimum of fertilization.

Composition of the Ash.

The ash of the peeled root and the bark of the root were subjected to analysis, with the following results:

ANALYSES OF THE ASH OF CASSAVA ROOT.

Constituents.	Peeled Root.			Bark of Root.		
	A	B.	Mean.	A.	B.	Mean.
Carbon,	0.30	0.31	0.31	0.79	0.77	0.78
Silica (soluble in solution of Na_2CO_3),	0.97	0.91	0.94	10.53	11.36	10.94
Silica (insoluble in solution of Na_2CO_3),	7.15	7.15	7.15	52.99	52.16	52.58
Ferric oxid (Fe_2O_3),	0.66	0.66	0.66	2.46	2.44	2.45
Calcium oxid (CaO),	10.63	10.64	10.64	6.58	6.65	6.62
Magnesium oxid (MgO),	7.36	6.35	7.35	3.31	3.33	3.32
Sodium oxid (Na_2O),	1.12	1.28	1.20	0.84	1.05	0.95
Potassium oxid (K_2O),	41.72	41.54	41.63	14.73	14.68	14.70
Phosphoric acid (P_2O_5),	15.58	15 59	15.58	2.44	2.46	2.45
Sulphuric acid (SO_3),	3.67	3.80	3.73	1.71	1.71	1.71
Carbonic acid (CO_2),	9.15	9.12	9.14	2.53	2.50	2.51
Chlorine (Cl),	2.76	2.75	2.75	1.41	1.42	1.41
Total,	101.07	101.10	101.08	100.32	100.53	100.42
Oxygen equivalent to chlorine,	0.62	0.62	0.62	0.31	0.31	0.31
Difference,	100.45	100.48	100.46	100.01	100.22	100.11

From the above numbers it is seen that the ash of the peeled root is especially rich in potash, almost one-half of the total weight being composed of this substance. The potash is combined chiefly with carbonic and phosphoric acids. In the ash of the bark, as might be expected, silica is the predominant element, more than half the total weight consisting of this substance.

Assuming a yield of five tons of roots per acre, the weights of the important fertilizing materials removed by such a crop can be readily calculated from the data given.

Since the bark forms approximately 2.2 per cent. of the entire root, the total crop would be made up of the following amounts of bark and peeled root which would contain the amounts of mineral matter given below:

Peeled root,	9,780	lbs.,	containing	49.88	lbs.	ash.
Bark of root,	220	"	"	4 44	"	"
	10,000	"	"	54.32	"	"

The more important mineral matters contained therein are:

	Ash from peeled root, 49.88 lbs. Lbs.	Ash from bark, 4.44 lbs. Lbs.	Total ash from 5 tons, 54.32 lbs. Lbs.
Lime (CaO), ...	5.31	0.29	5.60
Magnesia (MgO), ...	3.67	0.15	3.82
Potash (K_2O), ...	20.77	0.65	21.42
Phosphoric acid (P_2O_5), .	7.77	0.11	7.88
			38.72

The less valuable mineral plant-foods, that is, those which are of so little note as to require no conservation or addition, amount to 17.60 lbs. per acre.

Quite a number of preparations was made from the starch of the root, and among them may be mentioned: First, tapioca; the first portions of starch washed out, especially, produce an excellent article of tapioca when moistened in the usual way. Second, glucose; both the fresh root and the extracted root yield full theoretical amounts of glucose, and samples of this article were made by the conversion of the starch both by sulphuric acid and diastase. The samples of glucose made from the starch were exceptionally good, especially when diastase was used; the glucose in this case containing large quantities of maltose. Commercially it would be more profitable to make the glucose directly from the fresh root, in which case the considerable percentage of cane sugar contained by it would be saved, whereas if glucose is made from the starch the cane sugar is previously washed out. On account of the presence of the bark, however, the glucose made from the whole root is not so fine in quality as that made from the pure starch. Third, alcohol; the glucose on fermentation affords the usual quantity of alcohol. Fourth, cane sugar; a beautiful preparation of cane sugar was made from the water used in washing out the starch. The amount of cane sugar, however, is not large enough to warrant its extraction on a commercial scale from the waters used for washing. It is, however, present in sufficient quantity to indicate that in making glucose it is better to use the whole root as indicated above.

The general result of the analytical work is such as to establish the fact that the cassava is a plant of high economic value and worthy of the attention of those interested in the carbohydrate products of the country.

REVIEWS AND REPORTS.

Recent Progress in Physical Chemistry, II.

The Theory of Solutions.

2. *Electrolytic solutions.*—The theory of electrolytic dissociation has recently been outlined in this Journal, **12**, 506; its development since that time includes discoveries of serious importance.

Ostwald has shown[1] how the basicities of acids, especially of the organic acids, may be directly determined from the electrical conductivities of their sodium salts. The conductivity of an aqueous solution of the salt, containing one gram-equivalent sodium in 32 liters, is observed; the increase of conductivity upon extending the dilution to 1024 liters (*i. e.*, halving the concentration five times) is always for salts of monobasic acids very nearly 10 units of conductivity; for those of dibasic acids, 20; of tribasic, 30; of tetrabasic, 40; of pentabasic, 50.

Examples given are:

	Diff.
Monobasic: Butyric acid,	10.2
Dibasic: Malonic acid,	20.6
Tribasic: Pseudo-aconitic acid,	29.6
Tetrabasic: Pyridinetetracarbonic acid,	40.4
Pentabasic: Pyridinepentacarbonic acid,	50.1

This singular regularity is due to the fact that at any given concentration the sodium salts of all acids of the same basicity have practically the same degree of electrolytic dissociation.

To determine the affinity-constants (dissociation-constants) of acids it is necessary to know their maximum molecular conductivities μ_∞, since the percentage dissociation (electrolytic) is given by $\alpha = \mu_v/\mu_\infty$, μ_v being the conductivity at any given finite molecular dilution v. They are found in the following manner[2]: We have $\mu_\infty = u + v$,[3] u and v being the migrating velocities of the positive and negative ions respectively. For strongly dissociated salts (as sodium chloride) μ_∞ can be directly measured. Further, we have the ratio of the concentration decrease at the anode to that at the kathode, upon electrolysis of a salt solution (as of sodium chloride), equal to u/v.[4] Combination of these values yields u and v, the migrating velocities of the sodium and chlorine ions. Subtracting v from μ_∞ for hydrochloric acid, a directly measurable quantity, yields the migrating velocity of the hydro-

[1] Ztschr. phys. Chem. **2**, 901. [2] Ostwald; Ztschr. phys. Chem. **2**, 840.
[3] F. Kohlrausch: Ann. der Phys. Wied. **6**, 167. [4] Hittorf (1853).

gen ion, and subtracting u from μ_∞ for the sodium salt of any organic acid yields that of the negative ion of the acid. The sum of these values is the required conductivity of the acid at entire dissociation, since $\mu_\infty = u + v$. μ_∞ for any sodium salt has been shown to be $\mu_{1024} + 2.4$, the readily ascertained molecular conductivity of one gram-molecule in 1024 liters, *plus* a small constant. Thus may be accurately determined the maximum conductivities of the acids, which are entirely inaccessible to direct measurement, and are yet necessary for finding the affinity-constants, *i. e.*, the dissociation-constants. From data thus obtained, and the molecular conductivities of the acids themselves, Ostwald and his pupils have determined the affinity-constants[1] of about five hundred organic acids[2] of the most widely varying types. The migrating velocities of the negative ions of different organic acids were found by Ostwald[3] to decrease rapidly with increasing number of atoms in the ion; the influence of additional atoms nearly disappearing, however, by about 12–15 atoms. It appeared further that isomeric ions have equal migrating velocities.

The conductivities of that typical electrolyte hydrochloric acid in solution in various organic solvents—benzene, xylene, hexane, ethyl ether, methyl, ethyl, isobutyl and isoamyl alcohols—have been studied by Klabukoff.[4]

The conductivities were in all cases slight, corresponding to the normal vapor-pressures, freezing-points, etc., of these solutions. The greatest conductivity by far was in the methyl-alcohol solution.

In the light of the theory of electrolytic dissociation, which refers the manifestations of acid character to the action of free hydrogen ions, the following observations of Pelouze and Gore[5] are of some interest: Anhydrous acids, being undissociated, have no free hydrogen ions, and, in fact, blue litmus paper remains blue when placed in concentrated sulphuric, acetic, propionic and valeric acids. It also remains blue in water, but if a paper be transferred from one of the acids to the water both turn red, the aqueous acid solution containing free ions. In nitric acid the litmus is at once reddened, but this acid conducts electrolytically and is hence dissociated.

An application of the theory of electrolytic solutions to physiological investigation has been made by F. A. Hoffmann[6] of Leipsic. A study of the velocity with which albumen is digested by pepsin solution, in the presence of acids, has shown it to depend directly upon the dissociation (affinity) of the acid employed. The digestion-velocities yielded, for hydrochloric, phosphoric, arsenic, citric and lactic acids, the regular order, and approximately the numerical value of the percentage dissociations. Sulphuric acid formed an exception, as it acted directly upon the albumen.

[1] See this Journal **12**, 5.
[2] Ostwald: Ztschr. phys. Chem. **3**, 170. Complete review of the literature in a paper by Walden: *ibid.* **8**, 433. [3] *Ibid.* **2**, 840. [4] *Ibid.* **4**, 429 (1889).
[5] See Marsh: Chem. News **61**, 2. [6] Schmidt's Jahrbücher **233**, 268.

The percentage dissociations of organic acids have been recently determined[1] in the following manner: On titrating alkali into acid solutions, in the presence of red lacmoid, the blue color of the lacmoid salt appears when the concentration of the hydrogen ions of the acid has sufficiently decreased to equal that of the lacmoid. So, the weaker the acid employed the sooner the blue color appears. The percentage dissociations thus obtained are in satisfactory agreement with the values calculated from the inversion-velocities and electrical conductivities.

The affinity-constants of a number of organic acids, dissolved in 50-per cent. alcohol, have been determined by Lellmann and Schliemann[2] by comparison with oxyanthraquinone. It and the acid to be studied were brought together with a base, and the amount of the salt of the reference-acid formed was determined by a photometric method. The relative strength of the acids was found to be not quite the same as in aqueous solution (from Ostwald's conductivity measurements). The relative avidities of different acids, *i. e.*, the ratio of the amounts of their salts formed, are given, and these values are approximately equal to the square roots of the ratios of the corresponding dissociation-constants, as is required by the dissociation theory. Attention has been called to this point by Arrhenius.[3] Further, the different salts of the reference-acid have the same absorption, the free acid an entirely different one. This behavior is very common, the absorption in the salt solutions is that of the anion, which is the same in all, that of the undissociated acid, being that of an altogether different substance, is different of course. The attention in reading the two papers cited is taxed with much that is due simply to a misunderstanding of the dissociation theory.

Ostwald has recently offered an explanation[4] of the fact that some weak dibasic acids, as succinic acid, may be readily titrated with a colored indicator, whereas certain stronger ones, as phosphorous or sulphurous acids, may not be. He assumes the negative electrical charge of the anion to be localized at that point from which the hydrogen ion has been dissociated, and that the appearance of this charge must hinder the appearance of another negative charge upon the same ion, *i. e.*, the dissociating of the second hydrogen ion of the dibasic acid, and so prevent the complete formation of neutral salt. If the two carboxyls be widely separated, as in succinic acid, this hindering effect is supposed to have so diminished that the neutral salt may be formed, *i. e*, the acid may be successfully titrated. This explanation accords with the facts cited, but hardly with the behavior of the acids of the oxalic acid series, which dissociate their "second hydrogens" ever less with increasing complexity.[5]

[1] Röhmann and Spitzer: Ber. d. chem. Ges. **24**, 3010.
[2] Ann. Chem. (Liebig) **270**, 204; *ibid.* **270**, 208.
[3] Ztschr. phys. Chem. **10**, 671. [4] *Ibid.* **9**, 553. [5] Trevor: *Ibid.* **10**, 349.

A simple experiment has shown that the velocity with which methyl acetate is catalyzed by aqueous acids is the same (within 1 per cent.) when the solutions have been made stiff by gelatine (*agar-agar*) as it is in pure water.[1] Also the diffusion-velocities of electrolytes have been found to be in gelatinized water practically the same as in pure water.[2] Both results were to be foreseen, since the partial pressures of the ions are uninfluenced by the addition of the colloid.

The rate of saponification of an ester is proportional to the concentration of the hydroxyl ions of the base used. From the saponification-velocities of inorganic bases with methyl acetate Bugarsky[3] has determined their relative dissociations to be: potash, 1.000; soda, 0.965; lithia, 0.972; baryta, 0.944; strontia, 0.915; lime, 0.911. The agreement with the figures obtained from the conductivities is excellent.

The affinity-constants of thirty organic bases have been determined by Walker[4] from the molecular electrical conductivities of their sulphates and hydrochlorides, as well as from the velocities with which the hydrochlorides catalyze methyl acetate in aqueous solution. This catalysis is effected by the acid set free by hydrolytic action, which decreases in amount on passing from weaker to stronger bases. Bases varying in strength from orthonitroaniline (=376) to quinaldine (=89.2) were investigated.

A discussion between Lothar Meyer and J. H. van't Hoff, upon the theory of solutions, has been brought to an abrupt termination by a most amusing reply of the latter.[5] He shows that all experimental material yet at hand confirms the fundamental law that the osmotic pressure follows the laws of gases. Further, the statement that the theory requires solutions of equal osmotic pressures to have equal freezing-point depressions in different solvents and equal relative decrease of vapor-pressures, is shown to be totally wrong, none of these three sets of solutions being equivalent in fact or in theory.

In a paper by Arrhenius,[6] the law of mass-action has been applied to the study of the equilibria in solutions containing several binary electrolytes (*i. e.*, homogeneous systems), and he has shown that these equilibria are entirely accessible from the dissociation-constants of each possible set of molecules present, since the equilibria depend upon the percentage dissociation of each set as represented by the equation of the dissociation-isotherm

$$Ck = c_1 c_2.$$

Here C, c_1 and c_2 represent the concentrations of the undissociated molecules and of each of the dissociation-products (ions) formed, and k is to be found from conductivity, reaction-velocity, etc. The state of equilibrium between the ions and the undissociated

[1] Reformatsky: Ztschr. phys. Chem. **7**, 34. [2] Voigtländer: *Ibid.* **3**, 316.
[3] *Ibid.* **8**, 398. [4] *Ibid.* **4**, 319. [5] van't Hoff: *Ibid.* **9**, 477. [6] *Ibid.* **5**, 1 (1890).

molecules, obtaining in a solution of a weak and a strong acid and their sodium salts, is calculated, according to the mass law, from the dissociation-constants of each set of molecules. From the resulting concentration of the dissociated hydrogen is then calculated the thereto proportional inversion-velocity of the action of the solution upon cane sugar, and results agreeing well with direct experiment are obtained. It is further shown, by combining the equations for the dissociation-isotherms of the various dissociation-reactions coming into play, that the so-called "avidity"—the ratio of distribution of two acids with a base—is equal to the ratio of the square roots of the dissociation-constants of the acids, or *approximately* to the ratio of the percentage-dissociations of the acids.

The formulæ are applied further to the phenomena of hydrolysis, *i. e.*, the decomposition of the salts of very weak acids or bases by water, whereby water must be treated as a very slightly dissociated electrolyte. An example of this hydrolytic action, which, be it stated, *demonstrates* the electrolytic partial dissociation of water into hydrogen and hydroxyl ions, is the hydrolysis of the alkali carbonates in the sense of the equation

$$Na_2 \mid CO_3 + 2H \vdots OH \gtrless 2Na \mid OH + H_2 \vdots CO_2;$$

the two weak acids, water and carbonic acid, are so slightly dissociated that only the alkaline reaction of the strongly dissociated sodium hydroxide appears. If we take the salt of a weak base instead of a weak acid, as aniline hydrochloride, for example, the reaction is of the same character,

$$C_6H_5NH_2 \mid Cl + H \vdots OH \gtrless C_6H_5NH_2 \vdots OH + H \mid Cl,$$

but here the two bases water and aniline hydroxide are so weak that the solution shows only the acid reaction of the strongly dissociated hydrochloric acid.

A third case may be realized if we take the salt of a very weak acid with a weak base, where all products are slightly dissociated, and hence their solution if sufficiently concentrated reacts neutral. Such would be a solution of aniline acetate.

The following theory of the equilibria in saturated salt-solutions —that is to say, of the solubility-equilibria of electrolytes—is a simple application of the principle of mass-action to the conditions of these heterogeneous systems and is due to the brilliant Nernst.[1]

The solubility of a substance depends upon its "solution-pressure."[2] In a saturated salt-solution one equilibrium is maintained between the solid salt and its undissociated, dissolved molecules, proportionality necessarily existing between their concentrations; a second equilibrium existing between these latter and the ions

[1] Nernst: Ztschr. phys. Chem. **4**, 372. For additional quantitative confirmation see Noyes: *Ibid.* **6**, 241.
[2] See This Journal **15**, 141.

into which they, on the other hand, are transformed, calls for proportionality between the concentrations of undissociated molecules and ions. The concentration of the solid remaining constant, the product of the concentrations of the ions is thus, at constant temperature in saturated solution, also required to be constant. Increasing the partial pressure of one of the ions, by the addition of another electrolyte with a common ion, causes then a partial precipitation of the dissolved salt, *i. e.*, a decrease of its solubility. Thus hydrochloric acid will precipitate chlorides from their saturated solutions, and silver acetate will likewise be precipitated by silver nitrate or a soluble acetate, but not appreciably by acetic acid, since the slightly dissociated acid contains free acet-ions in but minimum amount. This behavior is in every way analogous to the precipitation of ammonium chloride from its vapor by the addition of one of its dissociation-products. In the paper cited this relation is brought into strict mathematical form and is verified quantitatively by suitable experiments.

As a further application of the theory, the influence of eleven different chlorides upon the solubilities of thallous and lead chlorides has been studied[1] for the purpose of determining the degree of electrolytic dissociation of these chlorides. In passing from 0.2- to 0.03-normal solutions, the dissociation was found for hydrochloric acid to increase from 73 to 89 per cent.; for the chlorides of potassium, sodium and ammonium, from 65 to 89; for those of magnesium, calcium, barium, zinc, manganese and copper, from 62 to 82; for cadmium chloride, 32 to 60. From these figures far more satisfactory dissociation-constants were obtained for the chlorides of the univalent metals than from the electrical conductivities of their solutions. For the chlorides of the bivalent metals a constant was not obtainable.

Nernst's theory of the solubility of a compound in the presence of one of its dissociation-products has been successfully applied by Behrend[2] to alcoholic solutions of phenanthrene picrate, containing an excess of phenanthrene or picric acid. In his first paper it is further shown that, in saturated alcoholic solutions, the products of the concentrations of benzyl isoparanitrobenzaldoxime and paranitrobenzyl isobenzaldoxime, which are the dissociated components of a double compound, remain constant no matter what excess of one or the other component be present. This follows from the proportionality of the concentration of the undissociated double compound, to that of the undissolved solid with which it is in equilibrium (mass law), the concentration of the solid being of course constant; and the proportionality of the former concentration to that of the dissociation-products, with which it in turn is in equilibrium. The dissociation of the compound is very complete—about 90 per cent.—as was shown by special experiments. The solubilities were determined by a suitable analytical

[1] Noyes: This Journal **9**, 603. [2] *Ibid.* **9**, 405; **10**, 265.

method. Deducting the amount of undissociated compound present, a most satisfactory constant was obtained. The paper is a very neat contribution to the study of the equilibria in solutions of organic compounds.

An electrolytic synthesis of dibasic acids has been developed by Crum Brown,[1] the method consisting in the electrolysis of the ester salt of a dibasic acid, whereby CO_2 splits off from the anion, which then unites with itself to form the di-ester of a more complex acid. Thus, from malonic acid was prepared succinic acid:

$$COOC_2H_5.CH_2.\overline{COO} + \overline{COO.CH_2}.COOC_2H_5 = COOC_2H_5.CH_2.CH_2.COOC_2H_5 + 2CO_2.$$

In a paper on the aqueous solutions of double salts,[2] convincing evidence has been adduced for the distinction between true double salts, as the alums, which, not existing independently in solution, give the reactions of their components, and the salts of complex acids, as Na_2PtCl_6, which do not do so. This distinction has been clearly understood ever since the classical investigations of Hittorf, in 1859, on the phenomena of electrolysis, and in this paper the conductivities of these salt solutions have been shown to require the simple distinction indicated. It will be remembered that the same conclusion must be drawn from the diffusion experiments of Graham and Rüdorff, who found the components of the true double salts to diffuse independently, while those of the salts of the complex acids do not; and from the evolution of heat in the formation of the latter, while no thermal evidence for the formation of the former in solution is obtainable.

Other interesting work upon dissociation-phenomena has recently appeared, which, although by no means electrolytic, may be profitably considered in this connection. The vapor-densities of sulphur vapor between 467.9° and 606.0° C. have been determined, with the aid of the Dumas method, by Biltz.[3] His observations have been calculated by Riecke,[4] from the potential theory of Willard Gibbs; the result indicating that normal molecules, S_8 first appearing, break up into $S_6 + S_2$, the S_6 molecules dissociating in turn into $3S_2$ as the temperature rises. It will be remembered that above 800° the molecular formula of sulphur remains constant as S_2. It appears, then, that the normal molecule is S_8, but that the boiling-point of sulphur lies above the temperature at which dissociation begins. This view is beautifully confirmed by molecular-weight determinations at a still lower temperature, the boiling-point of carbon bisulphide, made by Beckmann with the aid of the boiling-point method.[5] A mean value of 261 was obtained; S_8 requires 256. One experiment gave 255.

The molecular weight of iodine dissolved in ethyl ether and in

[1] Crum Brown and Walker: Ann. Chem. (Liebig) **261**, 107.
[2] Kistiakowsky: Zischr. phys. Chem. **6**, 97. [3] *Ibid.* **2**, 920. [4] *Ibid.* **6**, 430.
[5] Beckmann: *Ibid.* **5**, 76 (1890).

carbon bisulphide, and that of phosphorus dissolved in carbon bisulphide, were likewise determined; the molecular formulæ found were I_2 and P_4, respectively.

The dissociation of nitrogen peroxide in solution in chloroform has been studied by Cundall,[1] the amount of dissociation being determined by a colorimetric method. The percentage dissociation increased with diminishing concentration and with rising temperature. Ostwald[2] has calculated the results according to the formula for binary dissociation, $\alpha^2/(1-\alpha)v = k$, and obtained a satisfactory constant, thus showing the dissociation in this solution to follow the same law as in the gas. The dissociation is here, however, far less in degree.

By application of the second law of thermodynamics, the effect of temperature change upon chemical equilibrium has been expressed in very simple form by van't Hoff.[3] In the familiar thermodynamical equation connecting pressure and temperature changes,

$$\left(\frac{\partial p}{\partial T}\right)_v = \frac{1}{T}\left(\frac{\partial Q}{\partial v}\right)_T,$$

the heat $\partial Q/\partial v$ added in unit increase of volume at constant temperature, decreased by the work $p.\partial v = p$ done in the expansion, whereby x per cent. of substance is transformed, is the *heat of reaction* involved $\left(\frac{\partial x}{\partial v}\right)\frac{q}{T}$, q representing the molecular heat of reaction. Eliminating Q above, and substituting for $\left(\frac{\partial \frac{p}{T}}{\partial T}\right)_v$ its value obtained from the gas equation $pv = [n(x-1)+n'x]$, n initial and n' transformed molecules being involved in the reaction, there results

$$\left(\frac{\partial x}{\partial v}\right)\frac{q}{T} = \frac{RT^2}{v}(n'-n)\left(\frac{\partial x}{\partial T}\right)_v.$$

By expanding and differentiating the Mass-Law equation

$$\frac{\left(\frac{x}{v}\right)^{n'}}{\left(\frac{1-x}{v}\right)^{n}} = K,$$

these differential coefficients of x are eliminated, yielding as final result,

$$\frac{\partial \log K}{\partial T} = \frac{q}{RT^2},$$

[1] J. Chem. Soc. 1891, 1076. [2] J. Chem. Soc. 1892, 242.
[3] Van't Hoff: Kongl. Sv. Vet.-Akad. Handlingar, **21**, No. 17; also Arch. neerl. **20**, 239.

the change with temperature (at constant volume) of the equilibrium-constant K, as function of the molecular heat of reaction q. Depending upon the character of the reaction, q may be the so-called heat of vaporization, of sublimation, solution, dissociation, or of any reaction more strictly chemical. The integral of this equation

$$\log_e K_2 - \log_e K_1 = \frac{q}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$$

has been used for calculating many various heats of reactions,[1] of which the following are examples:

Reaction.	$\delta\beta$ = change of	q calc.	q obs'd.
Vaporization of water.	vapor-pressure.	10100 cal.	10296 cal.
Dissolving succinic acid in water.	solubility.	6900 "	6700 "
Sublimation of ammonium hydrosulphide.	dissociation-pressure.	21550 "	21640 "
$BaCl_2 + 2H_2O = BaCl_2\,2H_2O$.	tension of water vapor.	3815 "	3830 "
$N_2O_4 = 2NO_2$.	(found from densities).	12900 "	12500 "

Le Chatelier[2] has reversed this procedure, by calculating the percentage dissociation of carbon dioxide (reaction $2CO_2 = 2CO + O_2$), at different temperatures and pressures, from the heat of combustion of carbon monoxide. The agreement with such values as are known is excellent, other values are

at 1000° and	1.000 atm.	0.06 per cent.
3000° "	1.000 "	40.
3000° "	0.001 "	94.

An attempt has been made by Arrhenius[3] to calculate the heats q of electrolytic dissociation of certain acids and salts in aqueous solution, by a direct use of the differential equation $\frac{\delta \log K}{\delta T} = \frac{q}{RT^2}$, setting for $\delta \log K$ the change of K between 18° and 52°, as determined from measurements of electrical conductivity. The heats of dissociation found in this way are in all cases strikingly small, rarely exceeding 1000 gram-calories, and are mostly negative. It may here be remarked that if q in such cases be zero, or nearly so, the electrolytic dissociation is entirely, or practically, independent of the temperature. Recent experimental results of the writer[4] have in fact shown this dissociation for all classes of organic acids to remain practically unchanged through a temperature range of 25° to 100° C.

According to the theory of electrolytic dissociation, the heat of neutralization of an alkali with an acid is a summation of the heats

[1] A critical collection of this material is given in Nernst (Dammer's Handbuch der anorg. Chemie, Allg. Teil), 311–318 (1892).
[2] Ztschr. phys. Chem. **2**, 782. [3] *Ibid.* **4**, 96; corrected results given *ibid.* **9**, 339.
[4] Trevor: *Ibid.* **10**, 338.

of dissociation of their undissociated portions and of that of the salt formed, *plus* the heat of formation of water from hydrogen and hydroxyl ions (the heat of electrolytic dissociation of water). From the above results, and the observed heats of neutralization, Arrhenius calculated this heat of dissociation of water to be 13520 gram-calories at 21.5°.

Still another important result has been yielded by the equation $\frac{\delta \log K}{\delta T} = \frac{q}{RT^2}$. It is evident that, since R and T are essentially positive quantities, $\delta \log K$ and q must have the same sign; *i. e.*, *if a reaction* { *absorb* / *evolve* } *heat it* { *advances* / *retrogrades* } *as the temperature rises.* This extremely important principle has been termed by van't Hoff "Principe de l'équilibre mobile."

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NOTES.

On the Spreading of Solutions in Filter Paper.

From the work of Schönbein, Bayley, Goppelsröder and others, it is known that when dilute solutions of salts are absorbed by porous paper, the water spreads beyond the dissolved substance: thus, when a drop of a dilute solution of potassium hydroxide falls on filter paper, it is found that the outer rim of the wet area responds to no test for the alkali, but contains water only. Furthermore, when several substances are present in the solution, some of them will spread over wider limits than the others. It appears from the present investigation that of two salts, the one which has the greater velocity of diffusion spreads more rapidly in the paper.

Emil Fischer and Edward Schmidmer make use of these facts in the study of certain double salts and other complex compounds.[1] Their apparatus consists of a glass tube 70 cm. long and 2 cm. inner diameter, in which are placed, end to end, six cylinders of porous paper, each 10 cm. in length. This tube is allowed to dip into the solution, so that the bottom of the lowest cylinder is wetted by it, and is left there until the liquid has risen so that the fifth cylinder is completely wetted; this usually requires from three to four days. The determination is then made by washing out the salts contained in one of the cylinders, generally the third, fourth or fifth, and analyzing the solution thus obtained, in the usual way.

[1] Ann. Chem. (Liebig) **272**, 156.

The following are the main results of the investigation:

A 10 per cent. aqueous solution of ferrous ammonium sulphate, $FeSO_4 + (NH_4)_2SO_4 + 6H_2O$, gave in the fourth roll:

0.0242 gram Fe_2O_3,

corresponding to 0.0169 gram Fe

and 0.0173 gram NH_3

If the proportion of iron to ammonia in the compound be taken as 1 : 1, then that found in the cylinder is as 1 : 1.686, proving that the ammonium sulphate had travelled farther than the ferrous sulphate, and, hence, that the double molecule was dissociated into ammonium sulphate and ferrous sulphate.

With a cold saturated solution of the same salt the proportion was

(1) as 1 : 1.004
(2) as 1 : 0.993

in two experiments.

Ferrous potassium sulphate and nickel sodium sulphate were investigated in the same way, the results being, in general, in accordance with the above, and showing that in dilute solution these salts suffer dissociation in a high degree; in concentrated solution, on the contrary, no evidence of dissociation can be observed.

A study of the double chlorides of mercury with sodium, lithium and ammonium shows that the first two are dissociated in a 20-per cent. aqueous solution, but not in an alcoholic solution of the same concentration, whereas the chloride of mercury and ammonium is not dissociated in either solvent.

Other investigators (van Bemmelen, Rüdorff and others) had already shown that the double salts of phosphoric and hydrocyanic acids, and of the polybasic organic acids, are for the most part not dissociated. An investigation by the present method leads to the same conclusion, the following salts being the ones used:

Sodium ammonium phosphate $HNa(NH_4)PO_4 + 4H_2O$, potassium silver cyanide $KCN.AgCN$, and potassium sodium tartrate $KNaC_4H_4O_6 + 4H_2O$. The compound of grape sugar with sodium chloride, $2C_6H_{12}O_6 + NaCl$, is found to undergo dissociation in a 10-per cent. solution in water.

The authors have also studied solutions in alcohol and acetone of naphthalene picrate $C_{10}H_8.C_6H_2(NO_2)_3OH$, and methylketol picrate $C_9H_9N.C_6H_2(NO_2)_3OH$, but find no evidence of dissociation in either case.

Finally, some experiments were performed for the purpose of comparing the present method with the older one used by Graham and Rüdorff, in which diffusion was allowed to take place through a membrane: the result goes to show that the older method is more rapid for aqueous solutions, but for solutions in alcohol the newer method is to be preferred, since in such cases diffusion goes on very slowly through a membrane. A. P. SAUNDERS.